THE DEVELOPMENT OF METHODS AND APPARATUS FOR THE PRECISE MEASUREMENT OF ELECTRICAL CONDUCTIVITIES WITH ESPECIAL ATTENTION TO THE REDETERMINATION OF STANDARD REFERENCE VALUES

By

ROBERT DEANE THOMPSON

A DISSERTATION

submitted in partial fulfillment
of the requirements for the degree of Doctor of Philosophy
in the University of Michigan
August 1936

PRINTED IN U.S.A.
EDWARDS BROTHERS, INC.
LITHOPRINTERS AND PUBLISHERS
ANN ARBOR, MICHIGAN
1936

ERRATA

Page	Column	Line	Now reads	Should read
iii		30	Potentiometer Decade	Potentiometer and the Decade
v		3	83	82
v		4	82	83
9	2	21x	0.1D and 0.1D	0.1D and 0.01D
11	2	9	1883 by Christie	1833 by Christie
13	2	6x	0.01 represents	0.01 ohm represents
19	2	20	S_3, S_4 and S_5	S_3 and S_4
19	2	32	R_s was merely in parallel with the galvanometer and had an inappreciable effect on its sensitivity.	R_s was effectively removed from the galvanometer circuit.
23	2	24	Table 7	Table 6
24	1	5	Table 8	Table 7
24	2	10	Table 6	Table 8
25	1	7	Table 6	Table 8
35	1	20x	to $\pm$0.0001%	to better than $\pm$0.0001 ohm
36	2	5x	$\pm$0.0003%	$\pm$0.0001%
71	2	9x	resistance R	resistance R_1
72	1	10x	$\Delta R/Z$	$100 \Delta R/Z$
107	2	30	33, 635-637(1912).	32, 1001-1002(1911).

Those line numbers marked x are counted from the bottom of the page.

THE DEVELOPMENT OF METHODS AND APPARATUS FOR THE PRECISE MEASUREMENT OF ELECTRICAL CONDUCTIVITIES WITH ESPECIAL ATTENTION TO THE REDETERMINATION OF STANDARD REFERENCE VALUES

By

ROBERT DEANE THOMPSON

A DISSERTATION

submitted in partial fulfillment
of the requirements for the degree of Doctor of Philosophy
in the University of Michigan
August 1936

PRINTED IN U.S.A.
EDWARDS BROTHERS, INC.
LITHOPRINTERS AND PUBLISHERS
ANN ARBOR, MICHIGAN
1936

R. UNIV.
BIBLIOTHEEK
LEIDEN

DEDICATION

To my loving wife Katherine for her constant interest, encouragement and patience as well as active cooperation.

ACKNOWLEDGEMENTS

It is with sincere appreciation that I acknowledge the advice and assistance of Professor Alfred L. Ferguson and Professor Lee O. Case under whose joint direction and guidance this work was carried out.

For the technical advice and hours of patient labor which resulted in some extraordinarily fine pieces of equipment, I acknowledge my debt of gratitude to Mr. Walter Mintel.

To the Ford Motor Company of Dearborn, Michigan, for the donation of the material for the shaft of the precision cathetometer and for the active cooperation of its Engineering Department in the problems of precise gaging, I hereby convey my appreciation.

* * * * *

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORY	2
Kohlrausch and Grotrian	2
Kohlrausch, Holborn and Diesselhorst	3
Modern Improvements in Conductivity Methods	3
Newberry	4
Eastman	4
Parker and Parker	4
Developments from 1924 to 1932	6
Critical Analysis of the Work of Parker and Parker	6
Jones and Bradshaw	7
Criticisms of the Work of Jones and Bradshaw and Parker and Parker	7
APPARATUS AND METHODS	11
INTRODUCTION	11
THE WHEATSTONE BRIDGE	11
History	11
The Design and Construction of the Bridge	13
The Technique of Resistance Measurements with the Bridge	15
Treatment of the Results of Measurements	15
Control of the Room Temperature	18
Calibration and Tests	18
The Calibration of the Potentiometer	19
Calibration of the Upper Dials	19
Calibration of the Lower Dials	20
Check of the Constancy of Total Resistance	21
Measurement of the Resistance of the Contacts and Connections	21
Conclusion	21
Calibration of the Decade Resistance Boxes and Revision of the Potentiometer Calibrations	21
Factors Involved in the Calibration of the Potentiometer Decade Resistance Boxes	22
The Accuracy of the Primary Standard Coils	22
Thermal Effects and Other Disturbing Factors	22
Experimental Results and Calculations	23
Discussion and Analysis of Results	25
Tests of the Resistance Boxes with Alternating Current	26
Calibration of the Vacuum Thermocouple and the Frequency Bridge	27
Tests Performed on the Oscillator	27
Conclusion	28
THE THERMOSTAT	28
Introduction	28
Description of the Thermostat	28
The Thermoregulator	28
The Relay and Vacuum Tube Control	29
Performance Tests on the Thermostat	29
MEASUREMENT OF THE TEMPERATURE OF THE THERMOSTAT	30
The Basis of Measurement	30
The Platinum Resistance Thermometer and Measuring Devices	30
The Thermometer Bridge	32
Design and Construction	32
The Calibration of the Thermometer Bridge Coils	35
Treatment of Results	36
The Calibration of the Slide Wire	38
Conclusion	38

Page

The Calibration of the Resistance Thermometer 38
Introduction 38
Calibration at the Ice Point 40
Introduction 40
The Technique of Calibration at the Ice Point 40
Results of the Ice Point Determinations 41
Calibration at the Sodium Sulfate Point 42
Introduction 42
Purification of Materials 43
The Technique of Calibration at the Sodium Sulfate Point 44
Results of the Sodium Sulfate Point Determinations 44
Calibration at the Steam Point 45
Introduction 45
The Technique of Calibration at the Steam Point 46
Apparatus for the Measurement of Barometric Pressure 47
Introduction 47
Description of the Barometer 47
The Cathetometer and Meter Bar 45
Introduction 48
Description of the Cathetometer 49
The Meter Bar and Its Support 51
Calibration of the Filar Micrometers 53
Performance Tests on the Cathetometer 54
The Measurement of Barometric Pressure 55
Results of the Steam Point Determinations 58
Conclusion 60
The Accuracy of Temperature Measurements at 25° 60
EQUIPMENT FOR THE PREPARATION OF SOLUTIONS 61
The Balances, Weights and Weighing 61
The Weighing of the Solute and the Solution 62
Treatment of the Results of the Weighings 63
Proof of the Accuracy of Weighing 64
The Preparation of the Conductivity Water 65
The Determination of the Conductivity of the Water 66
The Conductivity Cell and Its Calibration 66
Tests on the Water for Solutions 66
The Purification of the Potassium Chloride 67
Introduction 67
Chemical Purification 67
Purification by Fusion 68
Conclusion 69
THE METHOD FOR THE STANDARD VALUE CONDUCTIVITY DETERMINATIONS 70
THEORY OF DESIGN OF THE CELLS 70
Introduction 70
The Analysis by Washburn 70
The Adaptation of the Washburn Analysis 71
THE PREPARATION OF THE CELLS 73
The Glass Tubes 73
Testing of the Fabricated Glass Tubes 75
The Internal Lapping of the Tubes 75
The Treatment of the Ends of the Tubes 76
Introduction 76
The Method of Grinding and Polishing of the Ends of the Tubes 76
The Evaluation of the Cell Constants 77
The Measurement of the Average Gross Sectional Areas 78
The Determination of the Volumes 78

Page

The Determination of the Lengths of the Cells 79
The Assembly of the Conductivity Cells 80
DISCUSSION OF RESULTS 83
SUMMARY 82
TABLES 85
FIGURES AND DRAWINGS 96
BIBLIOGRAPHY 106

INTRODUCTION

Electrical conductance is a property of electrolytic solutions which has received intensive examination for more than seventy years. A great impetus to this study was provided between the years 1883 and 1887 with the development of the classical electrolytic dissociation theory by Arrhenius.[2] He postulated the disruption in solution of some of the electrolyte molecules with the production of electrically charged ions to which the peculiar properties of the solutions were ascribed. The developments in the theories of solutions since that time have been numerous and far reaching.

An important tool in the building of the theories of electrolytic solutions has been the measurement of electrical conductivities. At the present time, however, the measurements may be usefully applied only if carried out with a high degree of accuracy and precision. Kraus[48] has emphasized this in the discussion following a paper on "The Conductance of Aqueous Electrolytes" presented by Shedlovsky, Brown and Mac Innes before The Electrochemical Society in 1934 when he stated: "I think the thing to be emphasized is the importance of highly precise data in order to analyze the very complicated problem that we have in the case of all these solutions. Electrolytic solutions represent an interesting case; it is very easy to make fairly precise measurements but the value of such results is very low. On the other hand, if we have sufficiently precise data, it becomes possible to analyze our results and to arrive at a satisfactory conclusion as to what is going on ..."

Present-day practice in conductivity investigations involves a number of measurements, the most important of which are the measurements of the resistance of the filled conductivity cell, its temperature, the concentration of the solution and a calibration of the cell. This calibration of the cell consists in an evaluation of its dimension factor or "cell constant" as it is termed. In order to make this calibration, conductivity values for standard reference solutions are needed. A number of such values were first obtained by Kohlrausch and Grotrian[44] in 1875. They served as standards until 1898 when more accurate values for seven solutions were provided by the Reichsanstalt in Germany on the basis of the work of Kohlrausch, Holborn and Diesselhorst[46] of that institution. These determinations of 1898 remained as standards until 1924 when Parker and Parker[64] redetermined the values of three of the solutions. The Parker and Parker values were used in computing all of the electrical conductivity values for solutions which are included in the International Critical Tables.[29] From 1924 to 1932 further technical and theoretical improvements in conductivity methods appeared which rendered the Parker and Parker values somewhat uncertain. The degree of precision with which conductivities could be measured exceeded the accuracy of the Parker and Parker values. In 1932 it seemed highly desirable therefore to repeat the determination of the standard values and place the accuracy of conductivity values on a plane with the precision of their measurement.

This dissertation is concerned with the design, construction and testing of apparatus suitable for precise electrical conductivity measurements and with the developing of an improved method for the redetermination of standard electrical conductivity values.

- - - - -

HISTORY

The resistance to the flow of electricity which an object may offer depends upon the nature of the material and its dimensions. For a homogeneous conductor of uniform length and cross sectional area, the relations involved may be formulated as

$$R = \rho \frac{L}{A}$$

where R is the resistance, ρ is the factor dependent on the material and termed the resistivity, L is the length and A is the cross sectional area. In dealing with solutions it is more convenient to supplant resistance and resistivity by their reciprocals, conductance and conductivity. Thus

$$\frac{1}{C} = \frac{1}{K} \cdot \frac{L}{A}$$

where C denotes the conductance and K, the conductivity. A transposition of terms yield the familiar expressions

$$K = C \cdot \frac{L}{A} \quad \text{or} \quad K = \frac{1}{R} \cdot \frac{L}{A}.$$

Conductivity values rather than conductance values are quoted in the literature, and are expressed in reciprocal ohm centimeters if the resistance is measured in ohms, the length in centimeters and the area in square centimeters. In order to determine the conductivity of an electrolytic solution from the measured value of its resistance in a cell, it is therefore necessary to determine a dimension factor, the so-called "cell constant", represented in the expressions above by the ratio L/A. The direct evaluation of the cell constant of a typical cell by measurement of its length and cross sectional area is, however, an exceedingly difficult task. It is rare indeed that such a cell is of uniform internal area or that the electrodes are plane and parallel. Furthermore, when the electrodes are irregular in shape and also completely surrounded by solution, the analysis of the current distribution at the electrodes and in their immediate vicinity is a complicated mathematical problem.

An alternative method for the determination of cell constants involves the use of standard reference solutions of known conductivity. This method is used almost exclusively at the present time. Measurement of the resistance of a cell when filled with a standard reference solution permits the computation of the cell constant from the formulation given above. The values for the standard reference solutions, however, must be obtained in cells the constants of which are found either by direct measurements of the dimensions or by measuring the resistance when filled with a material of a known resistivity such as mercury.

Kohlrausch and Grotrian. In 1875 Kohlrausch and Grotrian[44] made measurements on zinc sulfate solutions to be used as reference standards. The first method for cell constant evaluation mentioned above was used with a straight glass tube as the cell and its constant was determined by weighing columns of water of measured length. From these weights and the density of the water, the volumes were computed. Since the lengths of the cylinders of water were known, calculations of the average cross sectional area became possible. Zinc electrodes were used with both alternating and direct currents, the resistance of a zinc sulfate solution was measured and its conductivity calculated. This solution was then used for the determination of the cell constants of two smaller cells having sealed in platinized platinum electrodes. These two cells were used at 0°, 18° and 40° for measurements on a variety of solutions. The Wheatstone bridge was used in making the measurements with an alternating current generator as the source of current and an electrodynamometer for determining the balance point.

Until 1898 the work of Kohlrausch and Grotrian served as the basis of conductivity measurements, the values for their various solutions being taken as standards. During the interval from 1875 to 1898 improvements in technique were made which

warranted a redetermination of the standard values. Kohlrausch and Grotrian made their measurements using the best technique and apparatus which was available and realized the highest possible precision and accuracy for that era. Developments appeared in the following years, many of them due to Kohlrausch himself, which served to increase the precision of conductivity measurements. Their absolute accuracy, however, was still largely governed by the values for the Kohlrausch and Grotrian solutions. In order to raise the accuracy to a level comparable with the precision attainable, a redetermination of the standard values was needed.

Kohlrausch, Holborn and Diesselhorst. The circumstances for a redetermination of standard values were ideal in 1895. Kohlrausch had recently been named Director of the Reichsanstalt. With two of his aides, L. Holborn and H. Diesselhorst, he made a thorough study of the problem and published the results in 1898[46]. At that time the Siemens unit of resistance had been superseded by the ohm and the temperature scale was more accurately defined by the hydrogen gas thermometer. Two primary cells were used consisting of straight glass tubes with removable platinum electrodes. The cell constants were determined by the direct method that Kohlrausch and Grotrian had used, but the accuracy was improved. As stated, it involved the weighing of columns of water which filled the cell through measured portions of its length. In this way the volume and in turn the cross sectional area were computed. Five electrolytes at several concentrations were measured at 18° with the primary cells. The same solutions were then used to calibrate a number of cells with sealed in platinum electrodes. These secondary cells were used in turn to investigate the variations due to impurities in the reagents and to measure a few more solutions, particularly potassium chloride in concentrations of 0.1, 0.02 and 0.01 N. Measurements were also made at 0°, 9°, 18°, 27° and 36° to determine the temperature coefficients of conductivity of the various solutions.

It is to be emphasized that these measurements like the earlier ones with Grotrian were made with the best equipment available and with great attention to detail. Kohlrausch had a remarkable appreciation of the various possible sources of error in conductivity measurements and many of the methods used to eliminate them were devised by him. He was the first to use alternating current[39,44] and the telephone receiver[40] in connection with the Wheatstone bridge. In addition to this means of reducing polarization effects, he demonstrated the effectiveness of platinization for the same purpose[41,43]. These methods are used almost exclusively at the present time for such measurements. The precision and accuracy of the measurements with Holborn and Diesselhorst were so high that they remained the ultimate reference standards for twenty-six years. In view of the fact that these years covered a period of marked developments and improvements in physical chemical methods, the continued use of these values stands as a marked tribute to their excellence.

Since the published article by Kohlrausch, Holborn and Diesselhorst[46] does not contain sufficient data, a complete critical analysis of the work is impossible. The values are quoted to only four significant figures and the accuracy probably does not exceed ±0.10%. It is difficult to tell from the data given if the error in the work is greater than that amount.

In 1898 Kohlrausch and Holborn also published "Das Leitvermögen der Electrolyte"[45] which contains a review and description of the methods, results and chemical application of electrical conductivity measurements. This work served as a practical guide as well as reference book for many years. In fact very few efforts were made to introduce any improvements until about 1916.

Modern Improvements in Conductivity Methods. That date ushered in an era which has not yet reached its conclusion. The focal point for accurate and improved conductivity methods shifted from Germany to the United States with investigators such as Washburn, Kraus, Parker, Morgan, Lammert, Curtis, Shedlovsky and Jones and his students largely responsible for the change. They subjected conductivity measurements to keen analyses both as to principles and practises and the result has been a marked increase in the accuracy and precision of such measurements. By 1924 the accuracy

had improved from the ±0.10% of Kohlrausch's day to approximately ±0.05% and by 1933 it was very near to ±0.01%.

During the period from 1898 to 1924 there appeared the monumental work (1) of Washburn[86] while at Illinois on the theory of the design of conductivity cells, (2) of Taylor and Acree[79,80,81] at Wisconsin in which especial attention was given to frequency effects, (3) of Parker[62,63] at Clark University who studied the effects of frequency and voltage changes and apparent variations in cell constants, (4) of Hall and Adams[22] at the Carnegie Institute in Washington who first introduced the vacuum tube amplifier for increasing the sensitivity of measurement, (5) of Morgan and Lammert[58] at Columbia and Vassar who made an intensive study of non-aqueous solutions, and (6) of Curtis and Grover[9] at the Bureau of Standards whose development of improved resistance coils was outstanding. In addition to these developments which were accompanied by a corresponding increase in the precision of conductivity measurements, Kraus and Parker[50] in 1922 discovered that some of the Kohlrausch and Holborn[45] alternative directions for the preparations of the 0.1, 0.02 and 0.01 N KCl solution were in error by amounts ranging from 0.10 to 0.54%. Cell constants determined with solutions prepared according to these alternative directions were therefore in error by considerably more than the ±0.10% accuracy of the Kohlrausch, Holborn and Diesselhorst solutions.

Newberry. Two inconclusive attempts were made before 1924 to reexamine the Kohlrausch values. The first of these was that of Newberry[61]. In 1918 this investigator measured a 1 N KCl solution by using direct current and making consecutive potentiometric measurements of the fall of potential and the current in a column of solution through which the current was flowing. The cell constant was found by direct measurements of the dimensions of the cell. He obtained a result 0.6% higher than the Kohlrausch value for the same solution. It is doubtful if his results have an accuracy which is very much better than this difference.

Eastman. In 1920 Eastman[12] published the results of a more careful study in which he used both direct and alternating currents. In the direct current measurement, which was carried out in a manner similar in principle to that of Newberry, the cell constant was found by a determination of the cell resistance when filled with mercury. Eastman obtained a result 0.11% lower than the Kohlrausch value for 1 N KCl at 25°C. and for H_2SO_4 of maximum conductivity, a value 0.18% lower than the corresponding Kohlrausch value. He claimed an overall accuracy in these measurements of ±0.05%. Using the same type of cells, but with alternating current, he measured 1 N KCl again and obtained a value 0.03% lower than the Kohlrausch value as compared with the 0.11% difference obtained with direct current. Eastman felt that the difference between the alternating and direct current results was not fortuitous, but fundamental. He considered that the effect was due to differences in the movements of ions when under the influence of steady or reversing electrical fields. He appreciated that his measurements did not represent the ultimate in accuracy and precision and suggested, therefore, that if an accurate redetermination of the Kohlrausch values were made, it should be paralleled by a direct current measurement of equal accuracy. The results of such measurements have not been published as yet.

Parker and Parker. In 1916 Washburn[86] had indicated the desirability of a redetermination of the Kohlrausch values. The existence of such facts as presented in the preceding paragraphs proved beyond a doubt that such an investigation was needed. The problem was attacked by Henry and Elizabeth Parker[64] who in 1924 published the results of their work at the University of Chicago. Measurements were made only with alternating current at 0°, 18° and 25°C. The results at 0° were obtained with four primary cells consisting of internally ground and polished glass tubes with minute openings in the walls for the introduction and removal of solution. The ends were closed by plane platinized platinum electrodes which were pressed tightly in place. The cell constants were found by direct measurements. The lengths were obtained by comparison with a standard invar meter bar. The volumes were computed from the weights of mercury required to completely fill the cells at measured temperatures. These results permitted the calculation of the average cross

sectional areas of the tubes, but provided no measure of variations in bore.

Potassium chloride solutions at three concentrations were measured. Parker and Parker suggested that a better expression for concentration than equivalent weights per liter of solution or normality would be equivalent weights per cubic decimeter of solution. Since resistance is partially defined in terms of the centimeter as the unit of length and since the dimensions of cell constants are the reciprocals of units of length, they logically felt that centimeters rather than the cube root of milliliters should be the length unit selected in defining concentrations. Since the centimeter and the cube root of the milliliter are not identical, this new unit of concentration, named "Demal", is slightly different from the older unit, "Normal". A 1 D solution is about 0.003% more concentrated than a 1 N solution so that for most laboratory purposes the two are the same. Parker and Parker measured 1 D, 0.1 D and 0.01 D KCl solutions at 0° in the primary cells. Their original intent was to keep the sum of all known errors below ±0.01%. They found, however, that the best they could realize was about ±0.02%. The principal causes for the increased uncertainty were (1) variations in the conductivities obtained with different cells which they ascribed to so-called "electrode effects", and (2) variations in the measured resistances at 0°.

Four cells of the pipet type as designed by Washburn[86] were sealed together to permit filling with a common solution, and used for measurements on other solutions at other temperatures. The cells were calibrated at 0° with 0.1 D KCl. The 0.1 N solution of Kohlrausch, Holborn and Diesselhorst was remeasured at 0° and the new values were on the average 0.114% lower. In this connection, the procedure of Parker and Parker is open to criticism. Kohlrausch and Maltby[47] had measured a variety of solutions after the work on standard solutions of 1898. Among these was 0.1 N KCl which differed slightly in concentration from the Kohlrausch, Holborn and Diesselhorst solution due to the use of a molecular weight of 74.608 for KCl instead of 74.59. The basis for the determination of the conductivity of this 0.1 N solution was the earlier absolute measurements. Consequently the accuracy attained could not be greater than that realized by Kohlrausch, Holborn and Diesselhorst. In fact three of the cells which Miss Maltby used were from the group of secondary cells of the absolute investigation. Parker and Parker stated that "the work of Kohlrausch and Maltby is of considerably greater accuracy than that of Kohlrausch, Holborn and Diesselhorst..." This cannot be a true statement of fact. Kraus and Parker[50] had originally calibrated the four pipet cells with the 0.1 N solution of Kohlrausch and Maltby at 18°. Parker and Parker calculated the cell constants at 0° from the data and made a comparison with the results obtained using 0.1 D KCl at 0°. The average difference indicated the Kohlrausch and Maltby value for 0.1 N KCl at 18° to be 0.145% too large. A variety of measurements were made on this 0.1 N KCl solution and a method established for correcting data which were based on the Kohlrausch and Maltby values for KCl solutions. Since the Kohlrausch, Holborn and Diesselhorst values were more generally available to experimenters, it would appear that Parker and Parker's efforts were slightly misdirected. Kohlrausch and Maltby did not feel that their work was of greater precision than the absolute measurements and definitely did not recommend any changes in the absolute values.

Unfortunately no measurements were made at 18° or 25° with the primary cells. Parker and Parker recommended that for highly accurate work, cell constants should be determined at 0° and then corrected to the temperature to be used, on the basis of the coefficients of expansion of the cell materials. The majority of conductivity measurements are carried out at 18° or 25° so such a method would necessitate the construction of an ice thermostat just for the calibration. If Parker and Parker had measured their various Demal solutions at 18° or 25°, such a procedure could be avoided. Values were quoted by them for these solutions at temperatures from 0° to 30° at 5° intervals, but the values at 0° were the only ones obtained by direct measurement. The balance were computed by an involved method based largely on the results of Kohlrausch and Maltby corrected as indicated by Parker and Parker. The only plausible explanation for the omission of these direct measurements seems to be lack of time for experimentation because the manuscript was submitted from the Leeds and Northrup Company

of Philadelphia where H. C. Parker was employed after their work at Chicago.

The Parker and Parker values were favorably received and generally accepted as being of greater accuracy than the Kohlrausch values. In the compilation of the International Critical Tables, all the values in the section dealing with electrolytic conductivities[29] were recomputed on the basis of the 1924 standard values.

Developments from 1924 to 1932. The period from 1924 to 1932 introduces the contributions of Shedlovsky at the Rockefeller Institute for Medical Research and of Jones and his students at Harvard. Shedlovsky[73, 74, 75] is responsible for many improvements in experimental technique and has also developed a type of cell which eliminates electrode effects such as Parker[62, 63] had observed. Jones undertook a series of exhaustive investigations on conductivity methods. In 1928 with R. C. Josephs[38] he presented a thorough study of the Wheatstone bridge as applied to conductivity measurements. On the basis of the findings of that work they designed the so-called "Jones Bridge" which has since been favorably received in many laboratories. It is simply a very precise Wheatstone bridge especially adapted to conductivity work. In this first paper, mention was made of work then in progress on the design of cells and the redetermination of the standard values by a new method. The second, third and fourth papers with G. M. Bollinger[33, 34, 35] dealt with the bridge accessories, the design of cells and the validity of Ohm's law for electrolytes. Parker[62, 63] had observed apparent variations in cell constants depending on the resistance of the solution in the cells. This he ascribed to adsorption of the electrolyte at the platinum black surfaces and consequent changes in concentration of the solution. Jones and Bollinger[34] demonstrated that the variations were due to faulty cell design. In the Washburn cells which had been used almost exclusively for precise work after 1916, parts of opposite polarity were brought into close proximity. The result was a shunting effect on the cell by a resistance and capacitance in series which served to reduce the apparent cell resistance. By changing the relative locations of these parts, Jones and Bollinger were able to reduce the "Parker effect", as they named it, to negligible magnitudes. This effect was responsible for the "electrode effects" which Parker and Parker had obtained in their work.

Jones and Josephs had also demonstrated conclusively that the helical slide wire such as Parker and Parker had used in their bridge was incapable of yielding accurate results with alternating current. The reason for this was the mutual and self inductive effects which were unsymmetrical except when the balance was exactly at the midpoint of the wire. The result of such inductive effects was a shift in the balance point from the position obtained when using direct current. The magnitude of the errors varied with different slide wires examined, but in all cases the errors were present and appreciable.

Critical Analysis of the Work of Parker and Parker. It is evident that the Parker and Parker determination is open to justifiable criticisms. As to the method of measurement employed, several points are involved. The measuring bridge was faulty in design as shown by the work of Jones and Josephs. The single temperature selected for the absolute measurements was not successfully realized as indicated by the more pronounced variations in the resistance readings compared with those made at 18° or 25°. Furthermore, neither the KCl nor the water used were subjected to rigorous purifications to insure the absence of error due to impurities from those sources. In addition to these objections to the method used, the primary and secondary cells were all of faulty design possessing the Parker effect in unknown amounts. The magnitude of the uncertainty introduced from this cause cannot be estimated since the necessary data is not contained in the published article. Variations of as much as 0.15% were experienced using the different primary cells at 0° for all three concentrations. How much of this can be traced to variations in cell temperatures and how much to the Parker effect or other causes cannot be determined. It is to be observed, however, that the cells of smaller internal diameter always gave lower conductivity values than those of larger diameter. This would indicate that the Parker effect was present and in variable amounts. Although Parker and Parker brought their data into closer agreement by application of a "difference" method

to the observations, it is unreasonable to suppose that such a procedure entirely eliminated the errors due to the Parker effect.

In the light of these facts it seemed highly desirable to undertake another redetermination of the standard values taking advantage of the improvements introduced in the period 1924 to 1932.

Jones and Bradshaw. After work had been in progress on this investigation for about a year, an article was published by Jones and Bradshaw[36] describing the redetermination carried out at Harvard by a new method. The principle used was not original with Jones and Bradshaw having been employed by Eastman[12] in his measurements on KCl and H_2SO_4. It consisted in the determination of the cell constants of a group of primary cells by measuring their resistances when filled with mercury. This was an excellent procedure since mercury is the material used to define the International Ohm. A number of secondary cells were prepared which were suitable for measurements on the KCl solutions of Parker and Parker. The secondary cells were calibrated by a series of intercomparisons with the primary cells. Measurements were then made on 1.0, 0.1 and 0.01 D KCl solutions at 0°, 18° and 25° as had been done by Parker and Parker.

The results obtained by Jones and Bradshaw are all higher than the Parker and Parker values by amounts ranging from 0.019% to 0.12%. The differences at 18° and 25° are less than at 0°.

In order to critically discuss the work of Jones and Bradshaw, it is necessary to outline the method in more detail. Five primary cells designated Z_1, Z_2, ... Z_5 were calibrated at 0° using direct current and a very precise Kelvin bridge. When filled with mercury, each cell had a resistance slightly less than one ohm permitting direct comparison with standard one ohm resistance coils shunted by fairly large resistances. If the mercury had been replaced by 1 D KCl solution, the resistance would have been about 160,000 ohms at 0° which would have been too large to measure accurately by the alternating current bridge method. Consequently two so-called Y cells were constructed having cell constants of about 1100 $cm.^{-1}$ so that the resistances when filled with 1 D KCl at 0° would be about 17000 ohms which could be determined with sufficient accuracy. Their constants were obtained by filling the Z and Y cells simultaneously with an approximately 6 N solution of H_2SO_4 which gave a resistance of about 20000 ohms in the Z cells and about 2000 ohms in the Y cells at 0°. All of these comparisons were made at 0°. Having calibrated the Y cells, they were used to measure 1 D KCl solution at 0°, 18° and 25°. Next a pair of N cells were calibrated by comparison with the Y cells using a common 1 D KCl solution. The constants of the N cells were about 100 $cm.^{-1}$ and 150 $cm.^{-1}$ and so were suitable for the 0.1 D KCl which was measured in them at 0°, 18° and 25°. Finally a pair of Q cells with constants of about 11.5 $cm.^{-1}$ and suitable for 0.01 D KCl were calibrated by comparison with the two N cells using 0.1 D KCl solution. They were used to measure 0.01 D KCl at 0°, 18° and 25°. In all the measurements at 18° and 25° the cell constants were calculated from the values obtained at 0° by considering the expansion of the glass used in fabricating the cells.

Criticisms of the work of Jones and Bradshaw and of Parker and Parker. In the light of the known uncertainties in the Parker work it is difficult to explain why their values are all smaller than the Harvard values. If the temperature of 0° was not realized by the Parkers, their measured resistances would have been too small and the conductivities too large. Likewise the Parker effect is due to a shunting effect on the cell which would render the apparent resistance less than the true resistance and hence yield conductivity values which were too large. Jones and Bradshaw did not attempt to explain the observed differences which are in the opposite sense from those indicated by the above discussion. H. C. Parker has suggested in a personal correspondence that possibly the Jones and Bradshaw cells never did attain a temperature of 0°. The cells were heavily coated with paraffin to a thickness of at least 5 cm. in all directions so that possibly the heat conduction along the lead wires added heat at a rate sufficient to keep the temperatures of the cells at about 0.04°. If that were the case, the Jones and Bradshaw values at 0° would be too large by about 0.08%. Such a correction, if

applied, would bring the two determinations into much closer agreement.

The existence of an unexplained difference between the determinations of Parker and Parker and those of Jones and Bradshaw demands further study in order to reach the solution.

In certain respects the Harvard methods are not of the best. The most serious objection is in the measurement of temperature. At 18° and 25° specially constructed mercury in glass thermometers were used. They had large, thin walled bulbs and greatly extended scales. Readings could be made to 0.001° and the thermostat was brought to within 0.001° of 18° and 25° as indicated by those thermometers. However, it is certain that the actual temperatures were not always that close to 18° and 25°. Mercury in glass thermometers are subject to a number of well-known sources of error such as sticking of the mercury thread, hysteresis of the glass and variations of reading with changes in external pressure which prevent the realization of the highest accuracy in thermometric work. Both before and after the publication of the Jones and Bradshaw article, the measurement of temperatures by mercury in glass thermometers was discussed by correspondence with the Bureau of Standards who indicated that an accuracy of 0.001° at that time was unattainable with such thermometers. The Jones and Bradshaw article was published on May 6, 1933. To quote from a letter of May 25, 1933 from the Bureau, "Your inquiry was concerning the attainment of an assured accuracy of 0.001° or better in the measurement of a temperature of 25°C. To our certain knowledge we have been unable to attain such accuracy with mercury in glass thermometers." The Harvard thermometers were certified by the Bureau of Standards and for that type the assured accuracy ranges from ±0.002° to ±0.005°. Since the temperature coefficient of conductivity for these solutions is approximately 2% per degree, the measured conductivities are therefore uncertain by amounts varying from ±0.004 to ±0.010%. If the temperatures had been actually within 0.001° of 18° or 25°, this uncertainty would have only been ±0.002%.

The KCl used by Jones and Bradshaw was prepared for weighing by fusion in air. A saturated solution of the salt gave a negative test for alkali with phenolphthalein. Such a test is not entirely conclusive since phenolphthalein does not give an appreciable color below pH 9. Since the water used in dissolving the salt probably did not have a pH greater than 6, about $1.1 \cdot 10^{-5}$ mols of KOH would be required to produce a pH of 9 in the solution, since the latter is essentially unbuffered. A saturated solution of KCl is about 4 N at room temperature. Consequently, two parts of KOH per million parts of KCl could be present without being detected by the phenolphthalein reaction. Calculations on page 68 demonstrate that such an amount of KOH would produce an error in the conductivity of 0.1 D KCl of 0.00035%. The percentage error would be essentially the same for 0.01 D or 1.0 D KCl solutions.

The conditions under which the fusion is carried out and the salt is allowed to cool apparently influence the extent of hydrolysis. Shedlovsky[75] pointed out in 1932 that he had performed fusions of KCl in air and obtained a detectable amount of hydroxide. This was shown by the pink fringe formed around a crystal when placed in a few drops of water containing a trace of phenolphthalein. This uncertainty in the extent of hydrolysis renders the Jones and Bradshaw technique questionable. The conductivity results obtained are probably uncertain by at least 0.0004% from this cause.

In this same connection it may be noted that Parker and Parker partially fused their KCl so that only the lower portion contained in the crucible melted. It is difficult to estimate the possibility of hydrolysis under these conditions or to the completeness of removal of occluded water from the crystals. Hydrolysis tends to yield too high results while the presence of occluded water would give too low results. It is probable that the latter effect predominated. This fact may partially explain the difference between the values obtained by Parker and Parker as compared with those of Jones and Bradshaw since the Parker values are all appreciably smaller in magnitude.

It was pointed out to Jones and Bradshaw by Wenner of the Bureau of Standards that when the primary cells were filled with mercury, the current distribution was probably different from what it was when they were filled with H_2SO_4 solution. The reason is that the resistivity

of mercury is only about eight times that of platinum whereas that of the H_2SO_4 used was about 200,000 times as great. With the cells filled with mercury and with direct current flowing, the electrodes did not function as essentially equipotential surfaces. Tests were devised to determine the magnitude of the "Wenner effect" and the results showed it to be appreciable. It varied with the dimension of the cells but on the average amounted to about 0.015%. The constants of the Z cells as determined were all corrected by the appropriate amounts. This source of error was not pointed out, however, until the work was nearly completed. Some of the Z cells had been broken or changed so that the Wenner effects in them had to be estimated by a comparison of their shapes with those of cells with measured Wenner effects. The existence of this correction introduces another element of uncertainty into the final results. Although the corrections were measured and applied, the primary cell constants were not as realiable as they would have been if such correction had not been needed. The error from this source is probably less than $\pm$0.001%.

Another fault to be found in the Jones and Bradshaw method is the possible accumulation of errors resulting from the extended series of comparisons. If the standard values could all have been determined in cells, the constants of which were obtained by direct measurements with mercury, an ideal situation would have been realized. This is demonstrated by the fact that the average deviation from the mean for the five primary cells when filled with mercury was in no case greater than $\pm$0.0002%. However, the measurements made when the cells were filled with solutions did not show such excellent concordance. In the calibration of the Y cells, each was compared with four of the Z cells. The probable error of the mean for Y_1 was $\pm$0.0005% and for Y_2 it was $\pm$0.0008%. Jones and Bradshaw, however, considered the values for the Y cells to be reliable to only a few thousandths of one per cent. A consideration of only the actual agreement between individual readings indicates a higher precision. Apparently some constant sources of error were involved which were not disclosed by them. The constants for the Y cells at 18° and 25° were calculated from the results at 0° taking into consideration the expansion of the glass.

When the N cells were compared with the Y cells, each N cell was calibrated against each Y cell so that four sets of values were obtained. The probable error of the mean for these four sets ranged from $\pm$0.001% to $\pm$0.003%. However, the mean values of the comparisons against Y_1 were greater than those against Y_2 by 0.005% for N_2 and 0.008% for N_4. Since the agreement between the comparison of the Y and Z cells was so good, it is difficult to interpret this discrepancy. Jones and Bradshaw recognized the difference, but offered no excuse or explanation for its existence. The accepted values for the N cells on the basis of the tabulated data alone are, therefore, reliable to about $\pm$0.003% whereas the actual uncertainty is probably somewhat greater, but by an indeterminate amount.

In the comparison of the Q and N cells a similar group of four sets of readings was made. The probable errors of the mean ranged from $\pm$0.0005% to $\pm$0.0012%. The values obtained against N_2 were 0.005% greater than those against N_4. The accepted values are reliable therefore to about $\pm$0.004% taking into consideration also the uncertainties in the values for the N cells.

The final results on the various KCl solutions were then obtained at 0°, 18° and 25° for the three concentrations 1.0 D, 0.1 D and 0.01 D. The probable errors of the mean values, as calculated from the tabulated data, for the 1.0 D solutions are $\pm$0.002% and for the 0.1 D and 0.1 D they are $\pm$0.001%.

Jones and Bradshaw did not offer a critical analysis of their own work nor did they indicate the probable accuracy of the results. Since a great many factors were involved in the determination of the final conductivity values, it is possible to make only an approximate estimate of the probable accuracy. The factors which must be considered include the observed variations in the determinations of the cell constants, the probable differences between the actual and the measured temperatures of the thermostat, the presence of KOH in the KCl, the errors in the determination of the conductivity of the solvent particularly for the 0.01 D solution, the systematic errors in weighing the salt and the solutions, the error in the measurement of the Wenner effect and the errors in the calibration of

the resistance bridge due particularly to the errors in the values of the standard resistance coils. When all these factors are considered, the probable errors of the mean may be estimated as ±0.008% for the 1.0 D, ±0.009% for the 0.1 D and ±0.015% for the 0.01 D. Since these figures are merely estimates, only moderate reliance may be placed upon them. The general conclusion may be drawn, however, that the Jones and Bradshaw results are probably accurate to ±0.01%. The Parker and Parker values are precise to about ±0.02 or 0.03%, but in the light of later studies as discussed above, they undoubtedly do not possess such a degree of accuracy.

The Jones and Bradshaw article does not contain any explanation for the differences between these two sets of standard values which vary from 0.02 to 0.12%. Jones, it is true, has indicated the defects in the Parker methods in earlier papers. No results have been obtained as yet based on the fundamental principle followed by the Parkers, namely, the determination of the cell constants from actual dimensional measurements. Until such results are presented, the Jones and Bradshaw values cannot be accepted unreservedly as being accurate to ±0.01%. In order to be of value, however, such measurements must be made with an accuracy equal to if not greater than that realized by Jones and Bradshaw. Since the mode of attack undertaken in this laboratory was based in principle at least on the Parker method, the completion of the work seemed even more highly desirable.

In 1933 after a consideration of the work of Jones and Bradshaw, it was decided to continue this investigation and attempt to find the explanation for the observed differences in the two sets of standard conductivity values. The final standard values have not yet been obtained, but the foundations have been laid which it is felt are sound and secure. The completion of the study should yield results of an accuracy equal to, if not better than those of Jones and Bradshaw.

* * * * *

APPARATUS AND METHODS

INTRODUCTION

The design, construction and testing of the apparatus for precise electrical conductivity measurements divided naturally into four sections, (1) the Wheatstone bridge and its accessories for resistance measurements, (2) the thermostat for temperature control, (3) the thermometer for temperature measurement, and (4) the equipment for the preparation of solutions. The development of an improved method for the redetermination of standard electrical conductivity values involves in addition the design and construction of the conductivity cells.

In approaching this problem, the ideal was adopted of attempting to reduce to $\pm 0.001\%$ the error in the final value for conductivity due to each component measurement. While it did not prove possible to attain this goal with respect to every contributing determination, the equipment developed has been shown capable of an accuracy in conductivity values superior to any at present available.

In the remaining portions of the dissertation, each piece of apparatus involved in this work is considered in turn. The order of treatment in general is as follows: (1) an introduction which is generally historical in nature wherein analysis and criticism are presented concerning the researches of previous investigators as they influence the choice of apparatus or procedure for the present investigation and illustrate the limits of accuracy which may be anticipated in the use of the equipment adopted; (2) a description of the method and apparatus selected for the present investigation; (3) a detailed description of the technique involved in the use of the unit in question; (4) an explanation, where necessary, of the method of treatment of results; and (5) a description of such tests as were applied to demonstrate that the apparatus functioned within the prescribed limits of accuracy.

THE WHEATSTONE BRIDGE

History. Although the actual measurement of electrolytic conductivities may be accomplished by a variety of methods, it is a well accepted fact that the alternating current bridge method is capable of yielding the greatest accuracy and precision. A consideration of other methods is, therefore, omitted. The Wheatstone bridge was invented in 1883 by Christie[13], but it was not until 1874 that it was applied by Kohlrausch and Grotrian[44] to measurements of electrolytic conductivities. Fundamentally, the ideal Wheatstone bridge consists of four resistances free from internal electromotive forces, inductance and capacitance connected as shown in Figure 1. The source of current S and the current detecting device G complete the hook-up. The bridge is said to be balanced when no current flows through G. Under these conditions the well-known relation results:

$$\frac{A}{B} = \frac{D}{C} ,$$

from which any one resistance may be calculated when the other three are known. As applied by Kohlrausch and Grotrian, the unknown resistance was that of the filled conductivity cell. The other three arms were adjusted until the bridge was balanced and from their values the cell resistance was calculated.

The necessity for the use of alternating current in Wheatstone bridge measurements of electrolytic conductivities is of course well known, for when current flows through an electrolytic solution, reactions occur at the electrodes which result in the production of electromotive forces in opposition to the applied electromotive force. These "back" electromotive forces are grouped under the general heading of polarization, Kohlrausch[39] demonstrated that if the current alternates rapidly enough, the reactions at the electrodes tend to reverse during

each half cycle resulting in a marked decrease in polarization. As a source of alternating current, Kohlrausch introduced into the bridge a generator known in Germany as the "sinusinduktor". As a current detecting instrument to indicate the position of balance, he employed the electrodynamometer.

With the passage of time, many improvements were made in the bridge methods. In 1880 Kohlrausch[40] suggested the use of an induction coil as a better and more convenient source of current and the telephone receiver which had been recently invented by Bell as a current detecting device in place of the electrodynamometer. The use of the telephone required currents of audible frequency in the bridge. He also proposed the use of the helical slide wire as two arms of the bridge permitting more uniform changes in bridge settings and therefore greater ease and accuracy in balancing the bridge. In a paper published in 1893 in defense of the alternating current Wheatstone bridge method, Kohlrausch[41] proposed the use of a variable condenser in parallel with the resistance of one of the arms of the bridge adjacent to the cell. He found that this considerably improved the sharpness of bridge setting. In 1895 Kohlrausch[42] described improvements in the Wheatstone-Kirchhoff bridge such as the addition of extension coils and a commutator for introducing extension coils of different values which made it especially adaptable to conductivity measurements. This type of bridge was the same in electrical principle as the simple Wheatstone bridge, but it possessed greater flexibility in use and was very compact and convenient.

The bridge as used in 1898 in the absolute determination of standard conductivity values by Kohlrausch, Holborn and Diesselhorst[46] represented the results of years of study by Kohlrausch. In one arm of the bridge the cell and a measuring rheostat were placed in series. A good resistance box made up the second arm and a slide wire such as Kohlrausch had described in 1895 completed the circuit. A balance was first obtained with the cell in place, then it was short circuited and the resistance box in the cell arm adjusted to again obtain a balance. The amount of resistance so added, corrected for any slight shift in slide wire setting, was a direct measure of the cell resistance. No condenser was used in this case. The source of current was an induction coil and the detecting device was a telephone receiver.

With a few modifications this type of bridge was the recognized form used in all precise work for nearly twenty years. Usually the measuring resistance box in series with the cell was removed and placed in the adjacent arm. The induction coil was gradually superseded by the microphone hummer and for precise work by the so-called high frequency generator and the Vreeland oscillator[83]. Air condensers came into general use as the best means of balancing the capacity effects introduced in the cell by polarization, thereby improving the accuracy of bridge settings.

The advances which began about 1916 and were mostly of American origin, include additional and pronounced improvements in the bridge and its accessories. The resistance coils used in all grades of resistance boxes were known to possess self inductance and capacitance in the windings to varying degrees. The presence of these effects introduces errors in the resistance measurements with alternating current which can be evaluated only with difficulty. Curtis and Grover[9] showed by a very thorough study at the Bureau of Standards that errors of 0.05% or more could be experienced with even the best of resistance coils. The final result of their work which was published in 1912 was the development of a new type of winding for resistance coils which served to diminish the inductance and capacitance. The Curtis coils were found to have the same resistance to direct and alternating currents within 0.001%.

It had been suggested by Taylor and Acree[80] in 1916 and proved by Jones and Josephs[38] in 1928 that the slide wire as used by Kohlrausch was not suitable for work of high precision. Their suggestion was to replace it by ratio coils of fixed resistance wound so as to be essentially free of inductance and capacitance. Jones and Josephs also found that commercial resistance boxes designed for alternating current use were in error by varying amounts for resistances of 10000 ohms or more. This error represents the difference between the direct current and alternating current resistances of the coils. The errors ranged from 0.002% to 0.020% and so were appreciable in precision work. They designed new boxes in which the errors were all less

than 0.003%.

In order to diminish capacity effects between observer and telephones, Wagner[84] in 1911 devised a scheme for indirectly bringing the telephones to ground potential. Jones and Josephs in 1928 adapted the "Wagner ground" to the conductivity bridge and found that it improved the sound minimum and increased the accuracy of the bridge reading.

The use of electromagnetic and electrostatic shielding came into use during this same period. Since electromagnetic shielding is difficult to accomplish successfully, Jones and Josephs have suggested that the best remedy is to remove the offending instrument a sufficient distance in order to produce negligible coupling with the bridge. Jones and Josephs also condemn the use of grounded metal plates for electrostatic shielding preferring to use none at all. Shedlovsky[73] has logically pointed out, however, that shielding is necessary to avoid shifting capacities caused by movements of the observer's hands and body and to eliminate electrostatic couplings with other parts of the bridge or nearby electrical equipment. The arrangement of the shields is very important, symmetry being desirable in so far as it can be attained. Shedlovsky completely shielded all susceptible parts of the bridge and accessories with grounded metal boxes and cables.

Washburn and K. Parker[87] in 1917 made a careful study of the telephones and found them to be superior to the alternating current galvanometer or any other type of balance detecting instrument then available. The sensitivity can be improved by mechanically tuning the diaphragms to the frequency of the current and by electrically tuning with a condenser in series with the telephones to balance the inductance in the coils.

An improvement in bridge sensitivity was obtained by Hall and Adams[22] in 1919 by vacuum tube amplification of the current to the telephones.

Many improvements have been made in the source of current during this period. Kohlrausch had pointed out that the wave form of the current-time curve should be sinusoidal to prevent unsymmetrical polarization effects. With the development of the oscillograph it was possible to examine the wave forms obtained with various current sources. Taylor and Acree[79] made such a study in 1916. They showed that the induction coil is entirely unsuited to accurate work. The chief objection is that it gives a pulsating current with a large number of overtones which tend to produce unsymmetrical polarization. A number of motor-driven alternating current generators and the Vreeland oscillator[83] invented in 1908 were also examined carefully. The latter was found to be preferable.

In 1919 Hall and Adams[22] suggested that vacuum tube oscillators delivering audio frequency currents were very well adapted to conductivity measurements. A number of years elapsed before they came into general use, but at the present time they have almost completely supplanted all other sources for precise work. Jones and Josephs were probably largely responsible for this change as they demonstrated clearly the superiority of the vacuum tube oscillator over the Vreeland type from a number of viewpoints.

The Design and Construction of the Bridge. The bridge and accessories for the present work were designed and built taking advantage of these experiences of other investigators. As pointed out earlier, in every phase of this study the attempt has been made to reduce all errors and uncertainties to sufficiently small magnitudes so that the influence of each of the many measured quantities on the final conductivity values shall not be greater than $\pm$0.001%. In measurements with an alternating current bridge this condition may be satisfied by designing the cells to have the optimum value of resistance. Since in precision work it is desirable to dispense with the slide wire, the lower limit of resistance is imposed by the fact that decade resistance boxes as obtainable at present are not reliable for measurements to less than 0.01 ohm. The upper limit results from the increase in inductive and capacitative effects, with consequent alternating current error, in and between the coils themselves as the resistance increases. The optimum value of resistance is 1000 ohms, since 0.01 represents the desired 0.001% of this quantity and as will be indicated later, a resistance of this magnitude may be measured with Curtis coil resistance boxes without introducing an alternating current error of more than 0.001%. It will also be

shown later that 1000 ohms is a convenient working value of resistance for the design of the conductivity cells for the standard value determinations. The bridge was also designed to permit measurements on a special cell for conductivity water having resistances as high as 50000 ohms. The upper limit of measurement was placed at 100000 ohms.

A diagrammatic sketch of the electrical circuit of the bridge is given in Figure 2; Figure 3 is a photograph of the assembly. In Figure 2 all pieces denoted R correspond to resistance boxes, all parts denoted C represent condensers and the parts designated S represent switches. The source of current is a vacuum tube oscillator and the detector is a two-stage vacuum tube amplifier with telephones. The Wagner ground is constructed according to the recommendations of Jones and Josephs.

The bridge proper departs from the ordinary type of Wheatstone bridge as used in conductivity measurements in that the cell is introduced into an arm of the bridge already containing resistance and capacitance. This arrangement makes it possible to determine the cell resistance by a substitution method which is inherently the most accurate type employable.

The various metal boxes visible in Figure 3 are the electrostatic shields indicated by the dotted lines in Figure 2. The various resistance boxes, condensers and switches are contained in these metal boxes all of which are grounded. Resistance R_1 is composed of two resistance boxes in series. One of these consists of a five-decade Curtis coil box manufactured by the Leeds and Northrup Company, and has a range of 1 to 100000 ohms variable by 1 ohm steps. The coils of this box were thoroughly sprayed with molten paraffin as recommended by Rosa and Babcock[72] in order to minimize changes in the resistances of the coils with humidity variations. The remainder of R_1 is a two-decade box produced by the Leeds and Northrup Company having a resistance range from 0.01 to 1.00 ohm in 0.01 ohm steps. The unit R_2 is a two-decade box of the same type as the large box in R_1, but having a range from 1000 to 100000 ohms in 1000 ohm steps. Item C_1 is a precision variable air condenser of maximum capacitance 1500 micromicrofarads. (General Radio Company, Type 222L). It has an internal shield connected to one of the terminals as shown in Figure 2. Condenser C_2 is also of the variable air type. It consists of a General Radio condenser (Type 246M) of maximum capacitance 3000 micromicrofarads, but it was remodeled by the Physics Instrument Shop of the University in order to make it a precision instrument. Resistors R_3 and R_4 are 1000 ohm Curtis coils contained in individual grounded metal shells. Resistors R_5 and R_6 are three-decade boxes from the Leeds and Northrup Company giving resistances from 1 to 1000 ohms in 1-ohm steps. Finally, R_7 is a 1.2 ohm variable slide wire resistor from the General Radio Company. The unit C_3 is a combination of two ordinary variable air condensers mounted in a shielded box and arranged with switches to be introduced singly or in series across R_5 plus R_7 or across R_6 as needed. Boxes R_5 and R_6 are only partially shielded, but all the other parts of the bridge except R_7 are completely housed in the grounded copper boxes. The ground lead is of heavy insulated copper wire fastened to a piece of copper plate buried several feet below the surface of the ground just outside the laboratory. All of the connections to ground are made through this lead. All of the connecting wires in the bridge are covered with grounded, flexible, metallic sheaths.

The oscillator, which is of laboratory construction, is housed in a grounded copper lined wooden box about two meters from the bridge. Connection to the bridge is made with a twisted shielded cable, the shield being grounded. The portion of the electrical circuit responsible for the oscillations is of the tuned plate circuit type as devised by Gunn.[21] The complete arrangement of the circuit is shown in Figure 4. The tubes are of the low filament current type. The oscillations are subjected to one stage of amplification before being passed to the bridge. The power output is controlled by the potentiometer P_1. Figure 2 indicates the reversing switch S and vacuum thermocouple V which are interposed between the output transformer and the bridge. The vacuum thermocouple serves to measure the current to the bridge.

The detector, which is also of laboratory construction, is contained in a grounded, galvanized iron box near the bridge. Its design is based upon suggestions contained in the RCA Radiotron Cunningham Radio Tube Manual, Technical Series No. RC-11. Figure 5 illustrates the hook-up. Most of the amplification is accomplished by the '57 tube; the two '47 tubes operating in push-pull supply the power to the transformer T_1 which in turn feeds into the telephones. The telephones may be tuned mechanically to be in resonance with the frequency of the current thereby increasing their sensitivity. This amplifier permits settings of the bridge to 1 part in 100000 with no difficulty even with currents as low as 0.002 or 0.003 ampere flowing through the bridge.

Although not a part of the bridge proper, reference should be made at this point to the frequency bridge used in

connection with it. Provision of this auxiliary equipment is necessary as will be shown later due to the fact that the computation of certain correction terms to the directly measured resistance requires a knowledge of the frequency of the oscillations.

The frequency bridge used in this connection is shown in diagram in Figure 6. It is of conventional design, set up and mounted on a wooden frame with the parts rigidly fixed with respect to one another. Arrangements were made by connection at switch S_1 of Figure 2 so that the power from the oscillator can be passed to the Wheatstone bridge or to the frequency bridge at will the latter being connected at terminals a of switch S_1. Likewise switch S_5 was arranged so that the telephones can be connected to the Wheatstone bridge amplifier or to the frequency bridge which is connected at terminals b of switch S_5. This latter bridge did not give a good enough minimum to permit the use of the amplifier in that circuit. With the set up as made, sufficiently high accuracy in frequency measurements could be attained however.

The Technique of Resistance Measurements with the Bridge. Before consideration of the treatment of data obtained with the bridge, a description of the method of use of the assembled apparatus including the adjustment of the Wagner grounding device is desirable. In principle the method consists in alternate adjustment of the resistance and capacitance of the bridge and of the Wagner ground until silence is obtained in the telephones. This first adjustment is made with the cell in place; the cell is then short-circuited and the balance reestablished by introduction of additional resistance and capacitance in the cell arm. The actual manipulations of measurement include the connection of the filled conductivity cell into the measuring arm of the bridge as shown in Figure 2, the oscillator and amplifier are turned on and S_1, S_2 and S_3 are closed to the left. Resistance R_1 is set at zero and R_2 adjusted to bring the bridge as near as possible to balance. Since the smallest steps of R_2 are 1000 ohms, the final adjustment of resistance is made by manipulating R_1. Condensers C_1 and C_2 are simultaneously adjusted with R_1 to realize the best tone minimum in the telephones. Switch S_3 is then thrown to the right and C_3, R_5, R_6 and R_7 adjusted to again obtain a minimum of sound. Switch S_3 is then thrown back to the left and C_1 and R_1 changed slightly if necessary. This reversal of S_3 and continued tuning of the bridge is carried on until the best sound minima have been found for both positions of S_3. With experience the operator can accomplish this in about three reversals. This adjustment of the bridge in conjunction with the Wagner ground serves to bring the primary winding of the input transformer to ground potential. It is impossible to obtain sharp tuning of the bridge unless this is done. Jones and Josephs have shown on the basis of theoretical reasoning that there must be no possibility of escape of current to or from the ground at this primary winding. It is essential therefore to have the transformer primary at ground potential without actually connecting it to ground. When S_3 is thrown to the left the transformer has no connection to ground yet it is brought to ground potential when S_3 is thrown to the right. Jones and Joseph have shown that if the bridge is balanced as well as possible for both settings of S_3, then the primary winding will be at ground potential in both cases, which is the desired condition. The readings of R_1 and C_1 are recorded after the bridge is balanced.

To obtain the cell resistance a substitution method is employed. For this purpose, a low resistance shunt of copper rod, measured as 0.0003 ohms, is then connected across the terminals of the cell. Items R_1, C_1, R_5, R_6, R_7 and C_3 are readjusted to obtain a new balance, but R_2 and C_2 are not touched. In this way, resistance and capacitance in R_1 and C_1 respectively are substituted for the resistance and capacitance of the cell. The repeated reversals of S_3 are of course followed in this case as well. The new values of R_1 and C_1 are also recorded.

Treatment of the Results of Measurements. It is evident that the changes in R_1 and C_1 found for the two cases described above serve as measures of the resistance and capacitance of the filled conductivity cell. The mathematical relations to be developed later demonstrate that under the majority of conditions experienced, the cell resistance may be obtained as the difference of

the recorded values of R_1. Since R_2, R_3, R_4, and C_2 were not changed from the first arrangement to the second, the impedances in those arms must have remained constant provided the frequency was unaltered. It follows as a corollary from the conditions shown by Jones and Josephs to be satisfied at balance, that the impedances in the cell arm must have also been the same in the two cases.

An understanding of the electrical characteristics of a conductivity cell is necessary in order to analyse the impedance of the measuring arm of the bridge when the cell is in place. According to Wien,[92] a filled conductivity cell which possesses small dielectric capacity, by virtue of its construction, may be treated as though it were a resistance in series with a capacitance. The capacitance is a result of the polarization effects which cannot be entirely eliminated, but may be considerably reduced by the various expedients which Kohlrausch devised and which are mentioned earlier in this dissertation. The resistance is not the true electrolytic resistance, but includes in series a small polarization resistance. Figure 7 serves to represent schematically the two arrangements in the cell arm. The terms R_a and R_b represent the two settings of R_1, C_a and C_b correspond to the settings of C_1, R is the true cell resistance, R_p is the polarization resistance and C_p is the polarization capacitance. In this development, it is assumed that the condenser C_1 is free of leakage and that resistance R_1 is free of inductance and capacitance. The direct current resistance of C_1 is greater than 10^9 ohms which is ample.

Any attempt to determine the values of R, R_p and C_p in terms of R_a, R_b, C_a and C_b is impossible unless the frequency of the current, ν, is taken into consideration. After trial of several methods of solution the most suitable from the standpoint of ease and accuracy in use was found to be a trigonometric solution of the vector diagram.

Conventional notations and concepts are employed in the development and reference may be made to textbooks on alternating current theory for their definitions. Figure 8 indicates the vectorial relationships between the various currents and voltages. The vector lengths and angles used are selected to illustrate the general relations rather than any specific case. As the treatment unfolds, it will become apparent that the only values actually needed are R_a, R_b, C_a, C_b and ν although a number of others will be involved as intermediates.

In the analysis of the problem, reference may first be made to Figure 8. In this figure the vector E represents the fall of potential across the cell arm of the bridge. The current I in circuit (a) is out of phase with E due to the presence of the capacitance C_a. The total current may be represented as the vector sum of the two currents I_1 and I_2. Current I_1 leads the voltage by 90° whereas I_2 is in phase with E. The angle α represents the phase displacement between the current and the voltage and must carry over to circuit (b) because the other three bridges arms are not altered in making that change. Current I_4 also leads E by 90°, but in general it is smaller than I_1 because C_b is usually smaller than C_a. Current I_3, unlike I_2 is not in phase with E due to the polarization capacity of the cell. The vector sum of I_3 and I_4 is I, the total current. Then I_3 may be obtained by vector subtraction of I_4 from I. The angles β and γ as indicated are useful in the further developments.

The admittance triangle for circuit (a) may now be drawn as in Figure 9a. A second admittance triangle may be drawn, this one for circuit (b) as in Figure 9b, where the impedance of R_b, R, R_p and C_p is denoted by Z_3. It is possible, however, to express Z_3 by an impedance diagram as in Figure 9c. For convenience $R + R_p + R_b$ may be denoted as R_x. From Figure 9c it may be seen that

$$R_x = Z_3 \cos \beta.$$

If Z_3 and β may be expressed in terms of R_a, R_b, C_a, C_b, and ν, the problem is solved. From Figures 9a and 9b,

$$\frac{1}{Z_3^2} = \frac{1}{R_a^2} + (\nu C_a - \nu C_b)^2$$

$$\text{or} \quad \frac{1}{Z_3^2} = \frac{1 + R_a^2 \nu^2 (C_a - C_b)^2}{R_a^2}.$$

Now $$\beta = \alpha - \gamma,$$

so that $$\cos \beta = \cos (\alpha - \gamma) = \cos \alpha \cos \gamma + \sin \alpha \sin \gamma.$$

But $$\cos \alpha = \frac{\frac{1}{R_a}}{\frac{1}{Z}}$$ from Figure 9a

$$\text{or} \qquad \cos\alpha = \frac{Z}{R_a}.$$

Also, from Figure 9a,

$$\frac{1}{Z_a^2} = \frac{1}{R_a^2} + \nu^2 C_a^2 = \frac{1 + R_a^2\nu^2 C_a^2}{R_a^2}$$

$$\text{so that} \quad \cos\alpha = \frac{1}{R_a}\sqrt{\frac{R_a^2}{1 + R_a^2\nu^2 C_a^2}} = \sqrt{\frac{1}{1 + R_a^2\nu^2 C_a^2}}.$$

$$\text{Similarly} \quad \sin\alpha = \frac{\nu C_a}{\frac{1}{Z}} = R_a\nu C_a\sqrt{\frac{1}{1 + R_a^2\nu^2 C_a^2}}.$$

From Figure 9b by the law of cosines,

$$\cos\gamma = \frac{ZZ_3}{2}\left(\frac{1}{Z^2} + \frac{1}{Z_3^2} - \nu^2 C_b^2\right)$$

$$= \frac{1}{2}\sqrt{\frac{R_a^2}{1 + R_a^2\nu^2 C_a^2}}\sqrt{\frac{R_a^2}{1 + R_a^2\nu^2 (C_a - C_b)^2}}\left(\frac{1 + R_a^2\nu^2 C_a^2}{R_a^2}\right.$$

$$\left. + \frac{1 + R_a^2\nu^2 (C_a - C_b)^2}{R_a^2} - \nu^2 C_b^2\right).$$

From Figure 9b by the law of sines

$$\frac{\sin\gamma}{\nu C_b} = \frac{\sin\varphi}{\frac{1}{Z_3}}$$

$$\text{or} \qquad \sin\gamma = Z_3\nu C_b \sin\varphi.$$

But, from Figure 9a,

$$\sin\varphi = \frac{\frac{1}{R_a}}{\frac{1}{Z}} = \frac{Z}{R_a} = \sqrt{\frac{1}{1 + R_a^2\nu^2 C_a^2}}$$

$$\text{so that} \quad \sin\gamma = \frac{R_a\nu C_b}{\sqrt{1 + R_a^2\nu^2 (C_a - C_b)^2}}\sqrt{\frac{1}{1 + R_a^2\nu^2 C_a^2}}.$$

Substitution of the expressions for $\cos\beta$ and Z_3 in the equation $R_x = Z_3 \cos\beta$ yields the result

$$R_x = R_a\left[\frac{2 + R_a^2\nu^2 C_a^2 + R_a^2\nu^2 (C_a - C_b)^2 + R_a^2\nu^2 C_b(2C_a - C_b)}{2 + 2R_a^2\nu^2 (C_a - C_b)^2 + 2R_a^2\nu^2 C_a^2 + 2R_a^4\nu^4 C_a^2 (C_a - C_b)^2}\right]$$

In general the terms in the squared brackets will be very much smaller than unity so that by taking advantage of the properties of small quantities, the equation may be simplified to

$$R_x = R_a[1 - \nu^2 R_a^2 (C_a - C_b)^2 (1 + \nu^2 R_a^2 C_a^2)].$$

The influence of the correction term by which R_a must be multiplied to give the value of R_x may be illustrated by some typical cases. With a cell filled with one of the standard value KCl solutions, R_a might be equal to 1000 ohms, C_a and C_b to 200 and 100 micromicrofarads respectively and with a frequency of 2000 cycles per second ν would be equal to 4000π. Under these conditions the correction term would equal 0.9999984. Consequently in such a case the error in assuming that R_x and R_a are equal is less than 0.001%.

Situations might arise in which a neglect of the correction term would be serious. For example if a cell had a resistance of 50000 ohms and C_a and C_b were 600 and 100 micromicrofarads respectively and ν were again 4000π, the correction term would equal 0.887 so that an error of 12% in R_x would be made by assuming that R_x and R_a were equal. In such a case the general form of the equation obtained above for the relation between R_x and R_a would be more accurate than the simplified form for the general equation yields a correction term of 0.828. A neglect of this term would introduce an error of 21% rather than 12% in the value of R_x.

At lower frequencies the correction term becomes smaller and the approximation that R_x and R_a are equal becomes more exact. For most work it is apparent, therefore, that since $R_x = R_b + R + R_p$ and R_x is essentially equal to R_a, the value of $R + R_p$ may be obtained by direct subtraction of R_b from R_a with no corrections needed except of course the calibration corrections of R_a and R_b.

Jones and Christian[37] have recently developed a graphical method of computing the value of R from measurements of $R + R_p$ at a number of frequencies. The final step in the treatment of the results of resistance measurements, therefore, involves the evaluation of R from a series of values of $R + R_p$. In the case of measurements on a neutral salt solution such as KCl, sufficient platinization of the electrodes may be employed to render the value of R_p negligibly small as evidenced by no change in the value of R_x with change in frequency. Under such conditions R would be equal to $R_x - R_b$ or the resistance of the cell could be calculated as equal to the required change in resistance in the measuring arm of the bridge corrected as described above when the cell was short circuited in the bridge network.

Control of the Room Temperature.

In order to attain the high degree of accuracy desired in the present investigation, it is necessary to control the temperature of the room in which the measurements are made. Two reasons may be cited for this. In the first place, owing to the relatively high temperature coefficient of electrolytic conductivity, it is of course necessary to immerse the cells containing the solutions in an accurately controlled temperature bath. Although the thermostat used for this purpose in the present investigation will be described in detail in a later section, it is sufficient at this point to indicate that the satisfactory performance of such a device within the required limits demands that its surroundings do not vary greatly in temperature. The second reason for the necessity of control of the room temperature lies in the fact that temperature changes also affect the accuracy of other measurements involved in the final conductivity values. The equipment used in these measurements which would be affected by temperature fluctuations includes (1) the various resistance coils in the alternating current bridge (2) the high precision barometer to be described later and (3) the meter bar used for length measurements which will also be discussed in later sections. The accuracy of temperature control required is much less than in the case of the solutions, but is nevertheless important in measurements of the high precision desired. For example, in the case of the resistance coils of 1000 ohms or more in the bridge, calculations show that the temperature must be controlled with $\pm$ 0.7° in order that the conductivity values may not possess an uncertainity of more that $\pm$ 0.001% from this cause. Calculations for the other pieces of apparatus indicate approximately the same allowable temperature variation.

Therefore, in order to control the room temperature the ventilators were closed, the steam supply to the radiators was cut off, a double layer of insulating board was placed over the windows and weather stripping was fastened around the door of the laboratory. Heat is supplied to the room by means of two chromel wire units in series operated by a magnetic relay. These have a power consumption of 690 watts. Cooling is provided by the circulation of tap water (manually controlled depending upon the external conditions) through several suitable units, the most effective of which is a rebuilt automobile radiator. Three motor driven fans are employed to circulate the room air past the heating and cooling units. The magnetic relay is controlled by a thermoregulator of novel design as shown in Figure 10. The bulb on the right contains ethyl ether, liquid and vapor, sealed from the atmosphere by the mercury limb. Since the vapor pressure of the ether is 537 mm. of mercury at 25°, the temperature selected as being most readily realized the year around, approximately 200 mm. of mercury pressure are needed to balance against the atmospheric pressure. The temperature coefficient of vapor pressure for the ether is about 20 mm. per degree at 25°. This provides more than enough variation to obtain the desired control. The most important factor is the time lag between the changes in air temperature and corresponding changes in the temperature of the ether. The two liter bottle and mercury seal serves as a familiar type of barostat. Changes in atmospheric pressure produce relatively small changes in the volume of air in the bottle and hence insignificant pressure changes in the mercury surface at a. The bottle is thermally lagged to assist in keeping the entrapped air at constant temperature, a necessary condition for successful operation.

It was found that in any particular locality in the room, such as near the Wheatstone bridge, the temperature can easily be maintained at 25° within $\pm$ 0.3°. The air circulation is hindered somewhat by the equipment in the center of the room preventing the realization of ideal control. Furthermore the four overhead incandescent lights for the room liberate sufficient heat to bring the temperature near them well above 25°. Fortunately all the apparatus is located relatively near the floor. No attempt is made to control the humidity although such a procedure would probably help considerably in maintaining the constancy of the various resistance coils which are exposed to the atmosphere.

Calibrations and Tests.

It has been indicated that the cells for the determination of the standard

conductivity values will have a resistance of about 1000 ohms when filled with the solutions to be measured. Since it is desired to keep the error in the conductivity values due to the error in each measured quantity at 0.001% or less, it is necessary to determine the actual values of the resistance coils within ± 0.01 ohm which is 0.001% of 1000 ohms. This requirement applies only to the coils in the measuring arm of the bridge as the values of the coils in the other arms of the bridge do not enter into the calculations of conductivity.

The various coils were compared with a set of standard Bureau of Standards type resistance coils. The latter are unsuited for use with alternating current as they are not wound to be free of inductance and capacitance. Consequently for the calibrations, direct current was employed in conjunction with potentiometric measurements. A steady current was passed through the coil being calibrated and the corresponding standard coil. The fall of potential across each was measured with a Wolff potentiometer. In order to leave no doubts regarding the accuracy of these measurements, the potentiometer was also calibrated in terms of the standard resistance coils.

The Calibration of the Potentiometer.

The calibration of the Wolff potentiometer, Figure 11, was carried out according to the recommendations of Wenner and Weibel[89] of the Bureau of Standards published in 1914. It consisted simply in the measurement, by means of an accurate Wheatstone bridge, of the resistance of the potentiometer coils in terms of certified Bureau of Standard type resistors. The complete arrangement of apparatus as used is shown in Figure 12.

In the remainder of this section the details of the apparatus and manipulations involved in the calibration of the potentiometer (Figure 11) are treated in four parts: (1) the calibration of the two upper dials comprising coils of resistances of 1000 and 100 ohms respectively; (2) the calibration of the three lower dials involving coils of resistances of 10, 1 and 0.1 ohms respectively; (3) the check of the constancy of the total resistances; and (4) measurement of the resistance of the contacts and connections.

Calibration of the Upper Dials. In this case a substitution method was employed. The set up used with reference to Figure 12 was as follows: arm A of the bridge was a four-decade resistance box of resistance 1 to 10000 ohms in steps; arm D consisted of a four-decade box, but with a step-wise range of 0.1 to 1000 ohms; arm B was a plug type box, range 0.1 to 10000 ohms. Arm C was the measuring arm of the bridge in which were inserted either (1) the potentiometer coil to be calibrated; (2) a reference coil consisting of a Bureau of Standards type calibrated resistance of 1000 or 100 ohms; or (3) the substitution coils, which consisted of the five-decade and two-decade resistance boxes mentioned in connection with the alternating current bridge. The remainder of the circuit was composed of the galvanometer and battery with the necessary switches (S) and auxiliary resistors (R). The latter includes a resistance R_s of 20000 ohms, a resistance R_d of 400 ohms and a slide wire rheostat R_4 of 1430 ohms for control of the bridge current. The switches S_3, S_4 and S_5 and the resistors R_s and R_d were mounted under oil on a bakelite panel. The reversing switches S_1 and S_4 controlled the direction of the current to the bridge and galvanometer respectively; the latter switch also made it possible to check the remainder of the set up for thermal or residual electromotive forces. Items R_s and S_3 were used to regulate the effective sensitivity of the galvanometer so that excessive deflections might be avoided. When S_3 was set in position (1), the setting of R_s determined the fraction of the fall of potential across R_s which was applied to the galvanometer. When S_3 was in position (2), R_s was merely in parallel with the galvanometer and had an inappreciable effect upon its sensitivity. The unit K_1 was a Griffith's thermoelectric key,[17] slightly modified and used under oil. When using this key the galvanometer circuit is closed at all times except at the instant the battery circuit is closed. In this way inductance or capacitance in the various coils have no influence on the galvanometer reading as they exert effects only when the current changes, that is, on opening or closing of the battery circuit at which time the galvanometer circuit is open. The effects are dissipated before it is closed again. Critical damping of the galvanometer was provided by adjustment of the resistor R_d. The galvanometer used, Leeds and Northrup, Type R-c, has a resistance of 45 ohms, an external critical damping resistance of 250 ohms, and a period of 5 seconds. Its normal sensitivity of 0.005 microamperes per mm. at 1 meter was increased by mounting it at a distance of 3.1 meters from the scale.

No difficulty was experienced with leakage currents. Thermal effects produced a shift in the zero point of the galvanometer of about 0.7 mm. on reversing S_4. Following the recommendations of

White,[90] copper or brass plates connected by copper wires were placed under the potentiometer, galvanometer, Griffith's key and the switch box. No plates were put under the bridge set up as the measurements were made satisfactorily without them. Since the potentiometer set up was more permanent in nature, it was deemed advisable to include the plates even though they possibly were not needed at the time.

The procedure for determining the resistances of the 1000-ohm potentiometer coil was as follows. Arm A of the bridge in Figure 12 was set at a nominal value of 9999 ohms and arm D at 999.9 ohms. Connection was made to the first of the fourteen potentiometer coils at its terminal on the panel of the potentiometer. All of the potentiometer coils are fitted with these terminals which are provided with small screws to hold the lead wires tightly in place thereby making the connection to the bridge. The bridge was then balanced by adjusting B. The nominal reading was about 10025 ohms. As a check on the connections to the potentiometer coil, the leads were unscrewed at the coil terminals and replaced several times and no change in the balance point was observed. The two resistance boxes for arm C were then substituted for the 1000-ohm potentiometer coil and the bridge balanced by adjusting their total value leaving the other three arms of the bridge undisturbed. This procedure was then carried out for the remainder of the 1000-ohm potentiometer coils, for the 1000-ohm certified Bureau of Standards coil and for the sum of the coils of the four lower valued potentiometer dials, namely 999.9 ohms. In every case the combination of resistances for the two boxes in series included the nine 100-ohm coils and the nine 10-ohm coils, the necessary variations in the resistances required being supplied by the 1.0-, 0.1- and 0.01-ohm decades. As a consequence, the variations in resistance of the potentiometer and the other coils so compared are expressible in terms of the differences in the values of the three lowest decades of the two substitution boxes which were connected in series in the C arm.

The data are then treated by first assuming that the nominal value of these three decades represent the true values within 0.01 ohm. Since the 1000-ohm certified coil had a value of 1000.01 ohms correct to ± 0.05 ohm and the nominal resistance in the two boxes required to balance it was 999.80 ohms, the sum of the nine 100-ohm coils and the nine 10-ohm coils is obtained by assuming the difference of 9.80 ohms to be correct and subtracting that amount from 1000.01 ohms. The resulting value of 990.21 ohms then represents a first approximation to the actual resistance corresponding to the nominal value of 990 ohms. Applying this correction of + 0.21 ohm to the nominal reading of the two boxes, first approximation values for the resistances of the 1000-ohm potentiometer coils were calculated and are tabulated in the third column of Table 1.

The 100-ohm potentiometer coils were measured in a similar manner except that the resistance in arm A of the bridge was set at a nominal value of 999 ohms and arm D was set at 99.9 ohms. The nominal value of arm B was about 1002.0 ohms. In addition to the nine 100-ohm potentiometer coils, the 100-ohm certified Bureau of Standards coil, and the sum of the three lowest dials of the potentiometer were measured. In every case the combination of resistances from the two substitution boxes in series included the nine 10-ohm coils, the necessary variations in resistance being provided by adjustment of the 1.0-, 0.1- and 0.01-ohm decades. The treatment of the data was the same as in the case of the 1000-ohm coils. The 100-ohm certified coil had a value of 99.999 ohms correct to ± 0.005 ohm. As before, if the value of the three lowest decades of the two substitution boxes in series is assumed to represent the true values within ± 0.01 ohm, the observed value of 9.96 ohms may be subtracted from 99.999 to yield the value of 90.04 ohms as a first approximation to the actual resistance corresponding to the nominal value of 90 ohms. Applying the correction of + 0.04 ohm to the nominal value of the two boxes in series, first approximation values for the resistances of the 100-ohm potentiometer coils were calculated and are tabulated in the third column of Table 2.

Calibration of the Lower Dials. In the case of the small resistance coils of the potentiometer, Wenner and Weibel indicate that the substitution method is unnecessary, the simpler, direct method being of sufficient accuracy for the purpose. Accordingly the bridge was rearranged for this portion of the calibration. Arm A now consisted of a 1000-ohm unmounted Curtis coil resting on a block of paraffin, arm D was a similar 100-ohm coil resting on paraffin, arm B was composed of the two resistance boxes in series which had previously been used as the substituents in the measurements on the 1000- and 100-ohm potentiometer coils and arm C comprised the various lower valued potentiometer coils or the certified 100-ohm standard coil. The potentiometer coils were connected into the bridge at the terminals numbered 1 and 2 in Figure 11 and the various coils desired were introduced by setting the dials at the proper readings. Thus, in every case the measured resistance included the connecting wires between the three sets of coils. An inadvertent error was made in the measurements so that the nine 0.1-ohm coils were all included in measuring the 10- and 1.0-ohm dials. This however introduced no

complication as the subtraction of the value obtained with the 10-ohm dial and the 1.0-ohm dial set at zero and the 0.1-ohm dial set at nine gave in each case the resistance of those coils involved.

In order to compute the values of the potentiometer resistances from the relation $C = \frac{D}{A} B$, it was also necessary to determine the true value of the ratio of the resistance of the 100-ohm coil in arm D to the 1000-ohm coil in arm A. With the 100-ohm certified standard coil in arm C, the decade boxes in arm B were set at a nominal value of 1000.11 to balance the bridge. This 1000.11 ohms was made up of the nine 100-ohm coils, the nine 10-ohm coils and the remainder was obtained from the three lower decades. The first approximation values of the nine 100-ohm coils and nine 10-ohm coils of 990.21 ohms obtained from the substitution measurements when added to the remainder of the 1000.11 nominal ohms, namely 10.11 ohms, gave 1000.32 ohms as a first approximation to the value of B required to balance 99.999 ohms in C. The ratio of D/A as calculated is therefore 0.099967 rather than 0.100000 obtained from a consideration of the nominal values of D and A. Instead of multiplying each of the 27 values of B by 0.099967, 0.033% of those values were subtracted and the result multiplied by 0.1 to give values of C with sufficient accuracy. It was assumed that the two decade boxes in series had no calibration corrections when making the first approximation to the values of C. The values are tabulated in the fifth column of Table 3.

Check of the Constancy of Total Resistance. It is essential that the total resistance of any potentiometer remain constant while potential measurements are being made. The Wolff instrument is so constructed that this condition is established by an introduction or removal of compensating resistance as the settings for the three lower dials are changed. It is necessary to determine if the compensation is a real one or if it is so excessive or incomplete as to introduce appreciable errors into potential measurements. If the departure from the mean is greater than 0.1 ohm for any setting, then corrections must be applied. The checking of the constancy of the total resistance was found by setting the dials for the 1000-ohm and 100-ohm coils at zero and then measuring the resistance between the battery terminals for all the settings of the lower dials. The same bridge was used as for the measurements on the lower valued coils. The results are found in Table 4. The variation is seen to be $\pm$ 0.003 ohm in the total potentiometer resistance which is negligible as potentiometer settings may be made to only 0.1 ohm.

Measurement of the Resistance of the Contacts and Connections. Finally, to determine the resistance with all dials set at zero, that is, the resistance of all the connecting wires and contacts, the galvanometer key was left closed and terminals X or N of Figure 11 short circuited. A two volt battery in series with a resistance of 110000 ohms was connected at the battery terminals, the battery key was closed and the deflection noted. Then the 0.1-ohm dial was set at one and the process repeated. The results with the short circuiting link at either X or N connected into the circuit gave values ranging from 0.001 to 0.005 ohms, the average being about 0.0030 ohms, This was measured with all dials moved and then replaced at zero to check the constancy of the contact resistances. This correction for the resistance of the internal wiring and of the dial contacts is also seen to be negligible in comparison with 0.1 ohm.

Conclusion. The results of these calibration and testing measurements indicate that sufficiently high precision was attained in all of the measurements. In order to evaluate the absolute accuracy of the potentiometer coils, it becomes necessary to determine the exact values of the substitution box coils resistances employed in the above calibrations. As will be shown in the next section, these values are known to such a degree of accuracy as to render the values of the resistances of the potentiometer coils accurate to about 0.05 ohm.

Calibration of the Decade Resistance Boxes and Revision of the Potentiometer Calibration.

Since a given percentage of error in the measuring resistance of the alternating current bridge produces the same percentage error in the final value for the conductivity of the standard KCl solutions, the coils used as measuring resistances in the bridge should be calibrated to $\pm$ 0.001%. At the same time, owing to the fact that these decade coil resistances were used in conjunction with the potentiometer calibration, availability of their corrections make it possible to determine by successive approximations, making use of the potentiometer data, the values of the potentiometer coil corrections on an absolute rather than a relative basis, While it is true that for use of the potentiometer in the determination of potential differences, relative values of its resistances are sufficient, it is shown below that knowledge of the true resistances offers opportunity for valuable checks, by intercomparison, on the values of the Bureau of Standards reference coils.

The method used to calibrate the

decade coil boxes was the familiar potentiometric method in which the fall of potential is measured first over the unknown coil and then over a standard coil connected in series with it.

Factors Involved in the Calibration of the Potentiometer and Decade Resistance Boxes. The accuracy and precision of these measurements are subject to limitations due to: (1) uncertainty in the values of the primary standard coils; (2) such factors as thermal effects, contact and connection resistances, and leakage currents; (3) sensitivity of the various parts of the apparatus; and (4) the personal factor.

The Accuracy of the Primary Standard Coils. The accuracy of certification of the standard coils by the Bureau of Standards is ± 0.005%. Consequently the limit of accuracy of resistance measurements from the standpoint again of the knowledge of the resistances used is directly influenced by this uncertainty. However, the results of a number of measurements made during the calibrations indicate that the certified values are more accurate than ± 0.005%. This will be indicated in a later discussion.

Thermal Effects and Other Disturbing Factors. Thermal electromotive forces were experienced in the calibration of the lower valued potentiometer dials which served to slightly reduce the precision of measurement.

The cause of the difficulty was later traced to residual electromotive forces in the Griffith's thermoelectric key which probably were the result of strain introduced into the metal during the fabrication of the key. In order to balance this electromotive force, the bridge would have to be slightly unbalanced. With reversal of the current from the battery, the unbalance would have to be in the opposite sense. Consequently the observed difference in settings of the bridge represents twice the error due to this cause. When dealing with the lower valued resistances and consequently with smaller potential differences in the arms of the bridge, a greater degree of unbalance would be needed to offset the effect in the key. This is compatible with the observed result that the effect was undetectable for the measurements on the coils of 100 ohms or more. The magnitude of this lack of precision was not sufficient to warrant a recalibration of the potentiometer after removing the thermoelectric key. As far as the use of the potentiometer is concerned, the precision is ample as the measurements are not carried beyond settings to the nearest 0.1-ohm potentiometer coils.

For all of the coils involved in the various calibrations, the heating effects of the currents used were minimized by maintaining the power expenditures below the maximum advisable ratings suggested by the Leeds and Northrup Company for their Bureau of Standards type resistors.

Subject to the limitations as to the effect of excessive currents on the coil resistances, it is of course desirable, in the case of the resistance box calibration, to use as great a range of the potentiometer as possible. The fall of potential was therefore so selected as to give ample precision for the lower valued decade and the maximum precision for the higher. The values are given in Table 5. No variation in resistance could be observed on leaving the key closed for 15 to 20 seconds which was much more than the time employed in actual measurements, as then the key was simply tapped, deflection direction noted, key released, potentiometer adjusted nearer to balance, key tapped again, and so on to balance. If the current used were excessive, the resistances of the coils would tend to change in value due to the heat generated. In the case of the higher valued coils, because of the large resistance, the galvanometer sensitivity was very materially decreased with consequent reduction in precision of the measurements. Fortunately, however, these coils will not be used in the highly precise resistance measurements since the standard conductivity value cells will have in all cases resistances of about 1000 ohms while the cell for measurements on conductivity water although having a resistance of about 40000 or 50000 ohms, need be known accurately to only 2000 ohms in order that the final conductivity values should be accurate to ± 0.001%.

The large five dial box is so constructed that connection to each individual coil may be made at the terminals of the coil on the panel. These terminals have small holes to serve as mercury reservoirs so that contact may be made by dipping the ends of the potential lead wire into the cups. The current through the coils is introduced at the two binding posts on the panel. It is possible of course to measure the fall of potential between those contacts as well as at the terminals for each coil. The difference between the two measurements for a given coil, namely at the binding posts and at the terminals, is a measure of the resistance of the connecting wires in the box and the resistances of the decade contacts on the panel. With the two dial box such a determination could not be made as all the contacts are enclosed, connections being possible only at the box terminals.

In carrying out the computations to determine the corrections to the resistance box coils, the first approximations corrections were applied to the potentiometer readings and the values of

resistance then calculated by the relation.

$$R_2 = R_1 \cdot \frac{P_2}{P_1}$$

where R_2 is the resistance of the box coil being calibrated, R_1 is the resistance of the certified standard coil, P_2 is the sum of the resistances of the potentiometer coils needed in measuring the fall of potential across the box coil and P_1 is the corresponding sum for the standard resistance coil.

If an external current I_X is passed through a box coil and a standard coil in series, the falls of potential measured by the potentiometer may be expressed as

$$E_1 = I_X \cdot R_1,$$

$$E_2 = I_X \cdot R_2,$$

or $$R_2 = \frac{E_2}{E_1} \cdot R_1.$$

In this relation E_1 and E_2 represent the falls of potential across the standard coil and the box coil respectively and R_1 and R_2 represent the respective resistances of the same coils. Also if I_W is the working current of the potentiometer, and P_1 and P_2 are the total resistances of the potentiometer coils needed to obtain a balance with the standard coil and with the unknown respectively, then

$$E_1 = I_W P_1 \quad \text{and}$$

$$E_2 = I_W P_2 \ .$$

Therefore $$\frac{E_2}{E_1} = \frac{I_W P_2}{I_W P_1} = \frac{P_2}{P_1}$$

and $$R_2 = \frac{P_2}{P_1} R_1 \ .$$

The current I_W may be maintained sufficiently constant if the electromotive force of the standard cell remains constant to the same degree. This is a safe assumption regarding a good quality standard cell which may be readily checked by a test as to reproducibility. In this work an Eppley standard cell of the unsaturated cadmium type was used. The control of the room temperature to $\pm$ 0.3° is sufficient to insure that no appreciable changes occur in the electromotive force of the cell.

In the case of the 1000-, 100- and 10-ohm box coils, the current I_X was not as steady as might be desired, so in every case the potential measurements across both the box coil and the standard coil were made as rapidly as possible and in this order: standard coil, box coil, standard coil. In no cases did the standard coil measurements show a change of more than 0.00002 volt or 0.002% for the 1000- and 100-ohm coils and 0.02% for the 10-ohm coils. The mean value so measured for the standard coil was used in the calculations. The first unrecorded measurements made it possible to make the final measurements with the galvanometer always set for maximum sensitivity so no time was lost from that standpoint. Separate single pole double throw switches resting on paraffin blocks were used to throw from the standard coil to the box coil.

Experimental Results and Calculations. The internal lead resistances for the two dial boxes were calculated by the following scheme. The nominal values of resistance are given on the left and the measured resistances on the right of the equality sign.

$$(0.1) + (0.00) + \text{internal leads} = 0.114$$

$$(0.0) + (0.01) + \text{internal leads} = 0.020$$

The sum of these two equations is

$$(0.1) + (0.01) + 2 \cdot \text{internal leads} = 0.134$$

But $(0.11) + \text{internal leads} = 0.121$ by separate measurement. Therefore by subtraction, internal leads = 0.013 ohm. This result combined with four other similar measurements as recorded in Table 7 gave an average of 0.013 $\pm$ 0.000 ohm for the internal lead resistance of the two dial box. This result is useful in that it may be used in conjunction with the calibrated values for the ten settings of the 0.1-ohm decade when the 0.01-ohm decade is set at zero and for the ten settings of the 0.01-ohm decade when the 0.1-ohm decade is set at zero in order to determine the effective resistances for the one hundred and ten possible settings of the two decades. The result may be stated in the form of a rule: In using the two dial box, add the corrected values for the nominal resistances found in each decade and subtract 0.013 ohm from the sum to obtain the true resistance at the binding posts. In case one of the decade readings is zero, use the value for the setting of the other decade as representing the resistance at the binding posts.

When the two boxes were connected in series and all seven dials were set at zero, the total lead resistance was 0.029 ohm giving then the sum of the leads of the large box plus the leads of the small box plus the connecting wire. Subtracting 0.013 ohm for the leads of the small box yields 0.016 ohm for the leads of the large box plus the connecting wire.

The value of the lead resistances for the large box was found from a number of potential measurements made first at the binding posts and then at the terminals on the panel of the box. The results are given in Table 8. The average value is 0.010 ± 0.001 ohm. This value of 0.010 ohm when substracted from 0.016 ohm yields 0.006 ± 0.001 ohm for the connecting wire between the two boxes.

A measurement of these same values obtained by setting all the dials at zero and comparing the fall of potential across each part with the fall of potential across the one ohm standard coil gave 0.012 ± 0.002 ohm for the small box, 0.009 ± 0.002 ohm for the large box and 0.005 ± 0.002 ohm for the connecting wire. The agreement with the earlier figures of 0.013, 0.010 and 0.006 ohm respectively is satisfactory.

Since the procedure required for the computation of the corrections for the coils and potentiometer is somewhat involved, a brief outline of the steps followed is considered advisable. In this outline the 1000- and 100-ohm potentiometer dials are designated as "upper dials" and the 10-, 1.0- and 0.1-ohm dials are designated as "lower dials"; for the decade resistance coils, the 0.01-, 0.1- and 1.0-ohm coils are designated "small", and the 10- and 100-ohm coils "intermediate" and the 1000- and 10000-ohm coils "large".

(1) In the section on the potentiometer calibration, first approximations were obtained for the corrections to the potentiometer coils; those for the upper dials in terms of nominal values for the small decade coils, those for the lower dials in terms of nominal values for the small and intermediate decade coils. (2) From measurements described in the present section, first approximation values for the small decade coils were obtained by comparison with a certified standard 1.0-ohm coil by means of the potentiometer, making use of its approximate corrections. (3) From these first approximation values for the small decade coils and the potentiometer calibration data were calculated second approximation values for the upper potentiometer dials. (4) From these new values for the upper potentiometer dials and the first approximation values for the lower dials were calculated first approximation values for the intermediate decade coils. (5) From the first approximation values for both small and intermediate decade coils and from the potentiometer calibration data, second approximation values were obtained for the lower potentiometer dials. (6) Finally from the second approximation values for all the potentiometer coils and from the calibration data were calculated the corrections for the large decade coils.

In all cases approximation beyond the second gave no further changes in the corrections, therefore the second approximation values were adopted.

The actual experimental work in connection with the calibration consisted in the comparison by means of the potentiometer of the 1.0-, 0.1- and 0.01-ohm box coils with a 1.0-ohm coil which had a certified value of 0.99997 ohm. The first approximation values of R_2 for the various coils are tabulated in column 8 of Table 6.

When the corrected values for the 1.0-, 0.1- and 0.01-ohm decades of the two boxes are used to calculate the resistance added to the nine 100- and nine 10-ohm coils in calibrating the 1000- and 100-ohm potentiometer coils, it is evident the first assumption used therein is incorrect. This assumption was that the nominal values of the lower decades of the resistance boxes represented the true values with sufficient accuracy. In the case of the nine 100-ohm and the nine 10-ohm coils, 9.80 ohms was subtracted from 1000.01 ohms to yield 990.21 ohms. The value 9.80 ohms should be 9.814 ohms as measured which yields a difference of 990.20 ohms. When dealing with the nine 10-ohm coils, 9.96 ohms was subtracted from 99.999 ohms to obtain 90.04 ohms. The value 9.96 ohms should be 9.972 ohms which yields a difference of 90.027 ohms. The value of the nine 10-ohm coils by the second approximation is therefore 90.027 ohms instead of 90.04 ohms and the corresponding value of the nine 100-ohm coils is 900.17 ohms which is the same as the value used in the first approximation.

These new values with the corrected values for the lower decades were used to compute the second approximation values to the resistances of the 1000- and 100-ohm potentiometer coils. The results are given in Tables 1 and 2 and the changes are seen to be significant only for the 1000-ohm coils.

Using the second approximation values for the 1000- and 100-ohm potentiometer coils and the first approximations for the 10-, 1.0- and 0.1-ohm coils, the correct resistances for the 100- and 10-ohm box coils were found and tabulated in Tables 9 and 10.

In the measurements of the 10-, 1.0- and 0.1-ohm potentiometer coils, the 100-, 10-, 1.0-, 0.1- and 0.01-ohm resistance box coils were used. The first approximate values for the potentiometer coils were based on the assumption that the nominal values of the resistance box coils were sufficiently correct. When the corrected values for the resistance boxes as determined are used to recalculate the values for the potentiometer coils, the errors in the first assumption are seen to be appreciable only for the higher valued coils of the lower dials. The second approximation values for

the potentiometer coils have been tabulated in Table 3.

When the second approximation values are used to recompute the resistances of the box coils from 1.0- to 0.01-ohm, no appreciable differences can be detected as an examination of the results in Table 6 would serve to indicate. Therefore, the second approximation values to the potentiometer coils are essentially correct and may be used in calculating the resistances of the 1000- and 10000-ohm box coils. The resultant values are to be found in Tables 11 and 12. The 10000-ohm coils were appreciably in error by amounts ranging from 0.05 to 0.10%.

It may be concluded that the limit of precision of measurement for the 1000- and 100-ohm potentiometer coils is about ± 0.01 ohm, while for the 10-, 1.0- and 0.1-ohm coils the precision ranges from about ± 0.005 to ± 0.03 ohm.

In the case of the decade coils the precision of comparison of the 0.01-, 0.1-, 1.0-, 10-, 100- and 1000-ohm coils is about ± 0.001 ohm. For the 10000-ohm coils (which, however, will not be required in the precise conductivity measurements) the limit of precision is ± 0.2 ohm.

Discussion and Analysis of Results. As a check on the above calibration data, three sets of intercomparisons were made involving the potentiometer coils.

The sum of the nine 100-ohm, nine 10-ohm, nine 1.0-ohm and nine 0.1-ohm coils was found during the substitution measurements by comparison with the 1000-ohm standard coil to be 1000.298 ohms. Each of these decades was then measured separately against the lower valued standards. The sum of the values of the decades so obtained is 1000.280 ohms, a difference of 0.0018 ohm or 0.002%.

Another example may be drawn from the potentiometer calibration. The sum of the nine 10-ohm, nine 1.0-ohm and nine 0.1-ohm coils was found by comparison with the 100-ohm standard coil to be 99.927 ohms. The results of measurements on the individual decades gave a summation value of 99.903 ohms, a difference of 0.024 ohm or 0.02%. It will be recalled that the precision of determination of even a single 100-ohm coil was stated to be about 0.01 ohm.

A third illustration may be obtained from the potentiometer calibration. The first ten 1000-ohm coils were compared with the 10000-ohm standard coil by the substitution method and as has been indicated, the value of 10008.1 ohms was obtained. Each of these 1000-ohm coils was compared with the 1000-ohm standard coil. The sum of the values was 10008.10 ohms. The agreement here is better than 0.001%. The data for this particular comparison appears in Table 13.

A greater variety of intercomparisons were possible in the calibration of the resistance boxes. The ten 1.0-ohm coils were each compared with the 1.0-ohm standard coil and their sum was 9.995 ohms. Their sum was also compared with the 10-ohm standard coil and the result obtained was 9.996 ohms, a difference of 0.01%. It may be recalled that the precision of these measurements was 0.001 ohm.

The sum of the values of the nine 10-ohm coils obtained by comparison with the 10-ohm standard coil was 90.011 ohms. This same summation in comparison with the 100-ohm standard coil was found to be equal to 90.017 ohms, a difference of 0.006%.

The sum of the nine 10-ohm coils plus the ten 1.0-ohm coils in comparison with the 100-ohm standard was found to be 100.012 ohms. The values for the 10-ohm coils compared with the 10-ohm standard and the 1.0-ohm coils compared with the 1.0-ohm standard indicated above were respectively 90.011 and 9.995 ohms. The sum is 100.006 ohms or a difference of 0.006%.

The sum of the values of the nine 100-ohm coils obtained by comparison with the 100-ohm standard coil was 900.167 ohms. This same summation in comparison with the 1000-ohm standard coil was found to be equal to 900.17 ohms, a difference of less than 0.001%.

The sum of the nine 100-ohm coils, the nine 10-ohm coils, the ten 1.0-ohm coils and the internal leads of the large box was found to be 1000.184 ohms in comparison with the 1000-ohm standard coil. The sum of the various decade values plus the leads based on comparisons with the 100-, 10- and 1.0-ohm standard coils was 1000.183 ohms, a difference of 0.001%.

Finally the sums of the nine 1000-ohm coils, the nine 100-ohm coils, the nine 10-ohm coils and the ten 1.0-ohm coils were compared with the 10000-ohm standard and the value of 10010.6 ohms obtained. The sum of the values for the seperate decades when compared with the lower valued standards was 10010.7 ohms, a difference of 0.001%.

The results of comparisons involving the high resistance coils show smaller percentage differences than those for the low valued coils. Such a result would be anticipated when the methods of measurements are considered. The important point, however, is that the effect of any of the differences considered with respect to their influence on measurements of 1000 ohms is seen to be about 0.001%. Now if the 1000 ohm coil were in error by 0.005%, which

is the limit of accuracy given by the Bureau of Standards certificate, these various comparison measurements would demonstrate that fact. Since the accord is so much better than 0.005%, the error in the 1000 ohm standard coil must be less than 0.005%. A much more reasonable figure on the basis of these comparisons would be 0.002% or from a conservative point of view 0.003% rather than 0.005%.

The constancy of resistance of the standard coils is indicated by the two sets of certification values obtained in March 1934 and in April 1935. The values of each of the five standard coils agree to 0.001% showing, therefore, very slight aging effects.

These various intercomparisons also serve to indicate the accuracy of the measurements on the various potentiometer coils. The limiting factor is the accuracy of the certified value of the 1000-ohm standard coil, all other contributing factors being appreciably less than this. The results obtained indicate that potential measurements may be made with an accuracy of ± 0.00001 volt, such a difference in potential being the smallest amount directly measurable with the instrument.

An examination of the potentiometer data obtained in the calibration of the resistance boxes serves to indicate that the nominal readings of the potentiometer could be used to calculate the resistance coil values with the desired accuracy. Such a result was unpredictable before the calibration was carried out. In case it were desired to measure a wide variety of potential differences and to compare them accurately, then the corrections would probably need to be applied.

About nine months after the results presented above were obtained, the two resistance boxes were again compared with the same set of Bureau of Standards coils. The values obtained show negligible changes for the five lower valued decades. The 1000-ohm coils had all increased by about 0.002% and the 10000-ohm coils had increased by amounts ranging between 0.01 and 0.02%. It is necessary therefore to check the higher valued decades rather frequently for measurements to ± 0.01 ohm in 1000 ohms. During this second calibration it was observed that the contacts on the two dial box are not as reproducible in resistance as those of the five dial box which are of different construction. Variations of 0.003 ohm were experienced which is a rather high percentage of 0.01 ohm, but of course is a negligible percentage of 1000 ohms which is the resistance of the standard value cells to be measured with the alternating current bridge.

Tests of the Resistance Boxes with Alternating Current.

To determine whether the capacity between the resistance coils in the measuring arm of the alternating current bridge and the electrostatic shield caused an appreciable error in the effective value of resistance, comparisons were made between the alternating and direct current resistance of a test coil. This consisted of a 1000-ohm Curtis coil mounted on a bakelite panel and immersed in oil in a tin box. The unit was then placed in the thermostat shown in Figure 3. The value of the coil was measured at 1000 cycles with the bridge. The measuring resistance was set at 1001.987 ohms with the test coil short circuited and at 2.032 ohms with the coil in place so that its resistance was 999.955 ohms. The test coil was then potentiometrically compared with the 1000-ohm standard coil and its value was found to be 999.969 ohms. The difference, 0.014 ohm, is of the same order of magnitude as the precision of the direct current comparisons so it may justifiably be stated that in the measurement of a resistance of 1000 ohms, the alternating current bridge yields the correct value within ± 0.03 ohm, the limit of accuracy of the direct current calibration.

In order to prove that shielding was needed, measurements were made with the measuring arm unshielded. Movement of the hands above the box caused a distinct change in the sound intensity in the telephone receiver. With the shield in place no effect could be obtained by moving the hands about or touching the shield. That capacity to the shield did exist, however, was demonstrated by tuning to a minimum and then raising and lowering the cover for the large box. A distinct change in sound intensity was found indicating variations in the current in that arm of the bridge.

Curtis and Grover,[9] Jones and

Josephs[38] and also Shedlovsky[73] have pointed out that due to so-called end effects, the resistance coils of 10000 ohms or more should be disconnected when not in use. This point was tested for the two large boxes in the bridge. First all of the 10000-ohm coils except one were disconnected in the two decade box in the arm adjacent to the measuring arm of the bridge. This changed the apparent value of the first 10000-ohm coil by 0.07 ohm, or 0.007%. The 1000-ohm coil was then balanced by the appropriate amount in the measuring arm. The single appended 10000-ohm coil was removed and no shift in the balance point could be detected. Next, all but one of the 10000-ohm coils in the box in the measuring arm were disconnected and the balance for 1000 ohms shifted by 0.01 ohm. The single remaining 10000-ohm coil in the measuring arm was disconnected and no shift in the balance point could be detected for 1000 ohms. Since the maximum effect of the appended coils for measurements of 1000 ohms was only 0.001%, it was decided to leave the coils as mounted by the manufacturer. Accordingly the various connections were resoldered. These tests were performed after the first direct current calibrations were undertaken but before the second set. No appreciable change in internal lead resistance resulted from the testing.

Calibration of the Vacuum Thermocouple and the Frequency Bridge.

The development of the theory of resistance measurements for the determination of conductivity values indicated that the current passing through the bridge must necessarily be controlled within narrow limits in order to realize an accuracy of 0.001% in the measurements. The control of the current becomes possible only after a means for its measurement is provided. It was pointed out earlier that a vacuum thermocouple was installed for the purpose. This very compact and convenient device indicates the passage of current through it by the establishment of a difference of potential in the thermocouple which can be measured with a suitable device. In this case a direct current millivoltmeter was selected. The voltage generated in the vacuum thermocouple is applied directly to the millivoltmeter. Calibration was accomplished by passing measured direct currents through the vacuum thermocouple and observing the millivoltmeter deflections. The calibration data are given in Table 14. In practice these are plotted and a smooth curve drawn to permit interpolation.

It was also indicated earlier that in some cases a knowledge of the frequency of the current is necessary in order to calculate certain correction factors. The frequency bridge which was set up for this purpose and described earlier, was calibrated against a General Radio Oscillator, Type 377 B in the Electrical Engineering Department of the University, for measurements from 600 to 2500 cycles per second. The procedure consisted in determining the bridge settings for the various frequencies applied. A series of suitable graphs were prepared which permit interpolation in measuring any unknown frequency.

Tests Performed on the Oscillator.

The calibrated frequency bridge and vacuum thermocouple were used in performing tests on the operation of the oscillator. A voltmeter and potential divider were inserted to vary and measure the plate voltage applied to the oscillating tubes. A 22% reduction in plate voltage lowered the frequency by only 25 cycles per second at 1096 cycles per second. Such a voltage change is in excess of any experienced in normal operation. At 1865 cycles per second the same voltage reduction lowered the frequency by 52 cycles per second. With the oscillator adjusted for normal operation, frequency measurements were made with variations in power output. At 1091, 1882 and 2198 cycles per second the frequency changes did not exceed $\pm$ 2 cycles per second for 100% increases in power output. A third test was made under continuous operation. It was found that the oscillations reach a steady state very soon after turning on the filament currents. Measurements were made with a power output such as would be suitable for the precise measurements on standard solutions. During the course of an hour the frequency did not vary more than $\pm$ 3 cycles per second.

Rarely will it be necessary to know the value of the frequency within less than 50 cycles so that these tests indicate a more than satisfactory degree of stability

for the oscillator. The frequency as measured when the oscillator is connected to the frequency bridge will carry over with sufficient constancy to any measurements which are made with the alternating current bridge at about the same time and with approximately the same power consumption.

Conclusion.

As a result of the calibration and tests performed on the alternating current bridge and its accessories, it is evident that resistance measurements of 1000 ohms may be made with a precision of ± 0.001%. The accuracy is governed by the accuracy of the values of the calibrating resistors. The Bureau of Standards certification values for the standard comparison coils are stated to be accurate to only ± 0.005%. A variety of tests demonstrated that such an estimate is too conservative when the coils are not misused. For resistance measurements of 1000 ohms, the limit of error is nearer to ± 0.003% which will produce an uncertainty in the final conductivity values of the same amount.

THE THERMOSTAT

Introduction.

It was pointed out in the historical discussion that the temperature coefficient of conductivity of the various KCl standard solutions is about 2% per degree. In order to reduce the error due to temperature uncertainties and variations to ± 0.001%, it is evident that the temperature of the solution in the cell must be known to ± 0.0005° and maintained constant within those limits during the time of measurement of resistance. The simplest means of realizing these conditions is to submerge the cell in a constant temperature bath or thermostat. Jones and Josephs have proven conclusively that the use of water in such baths is inadvisable whereas a light grade of liquid petrolatum is entirely satisfactory.

Description of the Thermostat.

The basis of design of the thermostat constructed for this study for measurements at 25° was the type developed in this laboratory by Ferguson, Van Lente and Hitchens.[14] The tank shown in Figure 3 is of heavy sheet copper contained in an insulated wooden box which in turn is supported by an iron framework resting on castors. The tank measures 60 cm. from side to side, 54 cm. from front to back, and 41 cm. from top to bottom. It is filled within 5 cm. of the top with Standard Oil Company "Finol". About 150 liters of this oil are needed. Agitation of the oil is secured by means of two propellors each having four blades and mounted on a common shaft driven by a 220 volt direct current, 1/8 horse power, vertical drive Robbins and Meyers motor mounted at the back of the tank midway between the sides. The oil is forced toward the bottom of the tank where baffles direct it to the front, then upwards and finally across the top from front to back where it is again drawn down. The agitation is uniform and the flow is smooth in appearance except near the propellor shaft. Circulation of the oil in this manner was found essential for precise control. Cooling is accomplished by running tap water through a coil of copper tubing immersed in the oil. Heating is electrical, a unit of chromel wire wound on a bakelite form being placed near the cooling coil. Part of this unit is in continuous operation and the remainder is controlled by a thermoregulator and magnetic relay. In practice, the steady heating and cooling units are adjusted until the bath temperature remains at approximately 24.5°. The controlled heat is used to bring the bath up to 25.0°. It was found desirable to cool the motor and thereby minimize the transmission of heat along the motor and shaft mountings. For this purpose a coil of lead pipe, through which the tap water flows, was wound around the shell of the motor. In order to prevent the troublesome condensate of the humid summer weather from dripping off the cold pipes and into the oil, all exposed cold portions were wrapped with muslin strips and cups were mounted at the oil level to receive any water flowing towards the oil.

The Thermoregulator.

The thermoregulator was constructed from twenty-five feet of 1/4 inch seamless steel tubing. Extensive cleaning of this tubing was necessary before it could be used. This was accomplished by cleaning successively with 2:3 HCl, H_2O, 1:2 HNO_3, H_2O, a bristle brush and strips of muslin drawn

through, benzene, ether, acetone, clean muslin strips, strong soap solution, bristle brush, H_2O, clean muslin strips, acetone and dry air. At the end of this process the strips came through as clean as when inserted and as far as could be seen the inside of the tubing was bright and shiny. The two pieces of tubing which together made up the twenty-five feet were fitted with connections shown in section in Figure 13 by the Metal Processing Shops of the University and they were then flushed out with water, acetone and ether and dried.

To prepare the tube for filling, the pieces were joined, one end was connected to a vacuum oil pump and the other was partially closed by a steel plug with a small hole. The size of the hole was adjusted with de Kohtinsky cement until mercury would be drawn through into the tubing very slowly with the pump operating steadily. The tubing was mounted so that the plugged end was about 75 cm. lower than the other. The tubing was wrapped with a layer of asbestos and then with sixty feet of chromel C ribbon 1/16 inch x 0.010 inch. The 220 volts circuit was connected to this heater to warm the tubing and mercury and vaporize any last traces of moisture. The mercury used was first purified by drawing air through it while under concentrated H_2SO_4 for several days, then by washing in a Hildebrand tower[23] with $HgNO_3$-HNO_3 solution and with H_2O. It was finally distilled in a Hulett continuous still[24] and filtered through a pin hole in hard filter paper just before use. The plugged end of the tubing rested in a dish of this mercury during the filling. An hour and a half were needed to fill the tube, whereupon the plug was removed under the mercury with the pump still operating and a solid plug inserted and screwed in as tightly as possible. The tubing and mercury functioned as a barometer during these operations and therefore the mercury was prevented from sucking through into the pump when the plug was removed. The vacuum was then released and the plugged end removed from the mercury and tightened with a wrench. Upon shutting off the heat, the mercury slowly contracted so that during the cooling additional mercury was added dropwise at the upper or open end. The tubing was then coiled into a flat helix, fastened to a metal support and the glass head put in place.[14] This arrangement serves to locate the regulator about 3 cm. from the bottom of the thermostat and parallel with it. Although direct tests showed that the amount of gas still in the tube was very slight, it was sufficient to disturb the regulation of the bath when rapid barometric changes took place. Consequently, a barostat[14] had to be installed to maintain constant pressure on the mercury surface.

The Relay and Vacuum Tube Control.

The relay and heater circuits are shown in Figure 14. With the regulator connection open, the grid and plate voltages are adjusted to give 0.0 milliamperes plate current with a filament current of 0.20 ampere. When the regulator makes contact, the plate current increases to about 10.0 or 12.0 milliamperes which is ample for operation of the relay. The relay is of the type designed by Ferguson, but slightly modified. The soft iron core is suspended from the rocker arm by a two link chain rather than by a wire stretched over a wheel as in the original design. No trouble was experienced with stretching of the links until many months had passed at which time a slight adjustment of the screw at the bottom of the coil remedied the situation at once. The sensitivity of operation can be varied at will by means of three condensers in parallel with the 5.0 megohm grid leak shown in Figure 14. With no capacitance, the relay operates with a continuous chatter; with 0.02 microfarad in parallel, it trips from five to ten times per minute and with 0.05 or 1.0 microfarad the frequency is decreased to about one or two times per minute. In order to be free of the fluctuations in voltage of the 220 volt direct current lines, it was found desirable to operate the heater from a motor generator set.

Performance Tests on the Thermostat.

The fluctuations in bath temperatures are noted by means of the platinum resistance thermometer which will be considered in the following sections. The relay control grid circuit was set for moderately sensitive operation, that is, with 0.02 microfarad in parallel with the 5.0 megohm grid leak. A cell suitable for measurements on standard 0.1D KCl was placed in the bath. Thermometer readings were then made in the immediate vicinity of the cell. One test of four readings indicated an average deviation from the mean of $\pm$ 0.0003°. Another test of five readings indicated an average deviation from the mean of $\pm$ 0.0009°. Further tests demonstrated that other parts of the bath showed greater variations, but it was found that the regions near the conductivity cell maintain a very uniform temperature. Thus another test showed that for ten minutes the central region of the bath did not vary in temperature by more than 0.0007°.

From the results obtained it is evident that the thermostat will be capable of maintaining the region of the bath near the conductivity cell at a constant temperature within $\pm$ 0.001°. Due to the lagging effect of the glass tube constituting the cell, the fluctuations in temperature of the solution are appreciably less than $\pm$ 0.001°. They may be estimated to be very near $\pm$ 0.0005°, the desired condition. Such a variation corresponds to an uncertainty in the standard conductivity values of $\pm$ 0.001%.

MEASUREMENT OF THE TEMPERATURE OF THE THERMOSTAT.

The Basis of Measurement.

The temperature of 25°C. was selected for the standard value determinations because of its universal use at the present time in conductivity measurements. There is a decided disadvantage in using such a temperature because it cannot be realized directly as a fixed, equilibrium temperature such as the ice point or the steam point. Temperature measuring equipment which has been calibrated at two or more fixed temperatures must be used to determine the actual temperature of the system. However, by working at 25°C. many of the errors and difficulties introduced when making conductivity measurements at 0° or 100°C. are eliminated. This more than offsets the objections to the use of temperature measuring equipment and the attendent error of measurement at 25°. It is hoped that eventually these conductivity measurements will be carried out also at lower temperatures as well, as was done by Parker and Parker and by Jones and Bradshaw. H. C. Parker in a private communication suggested that the use of an air thermostat might prove desirable for the measurements at the lower temperatures.

The present basis of temperature measurement is the International Temperature Scale. The definition of this scale, fixed points on it and interpolating instruments for measuring temperatures other than the fixed points were all carefully selected in 1927 by the General Conference of Weights and Measures, an International body. This scale was selected as a practical means of realizing the Thermodynamic Centigrade Scale which is the fundamental basis of temperature measurement. The results and recommendations were presented in this country in 1928 by Burgess[4] who was the Director of the Bureau of Standards at that time. For measuring a temperature of 25°, the interpolation device is the platinum resistance thermometer. From 0° to 660° the relation of the resistance of pure platinum to temperature is adequately expressed by the equation

$$R_t = R_o(1 + A\,t + B\,t^2)$$

where R_t is the resistance at temperature t measured in degrees centigrade. R_o is the resistance at 0° and A and B are constants which may be evaluated by measurements of R_t at two other fixed points. There are three basic fixed points on the International scale for this region. The first is the ice point, 0.000°C., defined as the temperature of equilibrium between ice and air saturated water at normal atmospheric pressure. The second is the steam point, 100.000°C., defined as the temperature of equilibrium between liquid water and its vapor at the pressure of one standard atmosphere. The third is the sulfur point, 444.60°C., defined as the temperature of equilibrium between liquid sulfur and its vapor at the pressure of one standard atmosphere. In addition to these basic fixed points, a number of secondary points are recommended including the temperature of transition of sodium sulfate anhydrous to decahydrate, 32.38°C.

The Platinum Resistance Thermometer and Measuring Devices.

The platinum resistance thermometer was invented by Siemens[76] in 1871. However, it was not until the work of Callendar[6,7,8] and Griffiths[16,17,18] between 1887 and 1895 that successful forms were produced. At the present time there are two types suitable for precise work, the strain free and the calorimetric. The strain free type was developed by Callendar[7] and later improved by Sligh and by Dickinson.[77] The design permits heating the instrument to 660° without, as the name suggests, introducing appreciable strains in the wire which would change its resistance by distortion. The disadvantage of this instrument is its pronounced thermometric lag which cannot be avoided. The calorimetric type was designed by Dickinson and Mueller[10,11] to have a much smaller lag and is, therefore, more suitable for measuring fluctuating or drifting temperatures as experienced, for example, in calorimetry. In both types a coil of fine platinum wire is suitably mounted in one end of a sheath of glass or nickel tubing. Connection to the coil is made by platinum and gold wires which in turn are fastened to flexible copper leads at the thermometer head.

Since only the resistance of the platinum coil is desired, some means must be employed to eliminate or measure the lead resistances. There are three forms of thermometer construction which have been

devised for this purpose. These are shown in Figure 15. In the Callendar type, a pair of dummy leads, c - d, are placed alongside leads a - b to the point where they join the platinum coil. The measurements are then made with a Wheatstone bridge, leads c - d are connected in series with the measuring resistance in one arm while a - b and the platinum coil constitute an adjacent arm. In this way the resistance of a - b is compensated by c - d and the measuring resistance gives the value of the coil resistance directly. Likewise in the Siemens method, lead a is in series with the measuring resistances in one arm of a Wheatstone bridge, the coil and lead c constitute an adjacent arm and lead b is connected to the galvanometer. In this manner lead a compensates for lead c and the measuring resistance gives the value of the coil resistance directly. However, equality of the resistance leads and their contacts placed in the two bridge arms is essential in both cases in order to realize true compensation. This is a very serious disadvantage for two reasons: it is difficult to adjust the leads to equality when manufacturing the thermometer and there is no assurance obtainable that they change equally in resistance as the temperature of the thermometer changes. As a consequence, neither the Callendar nor Siemens construction are used for precise work.

A variety of methods of resistance measurements may be used with the four terminal type of thermometer shown in Figure 15, all of which are independent of the lead resistances. Sligh[77] has indicated the use of a potentiometer and current measuring shunt, a Kohlrausch differential galvanometer, a Thomson or Kelvin bridge, and the Wheatstone bridge with reversing commutator. Another scheme of measurement not mentioned by Sligh is the Smith difference method[78] which also utilized a Wheatstone bridge and reversing commutator. The maximum accuracy attainable by the potentiometer method is $\pm 0.01^{\circ}$ due to the limitations of potential measurements. It is therefore not used for precise determinations. The Kohlrausch differential galvanometer method is capable of a high degree of accuracy, but the galvanometer itself is extremely difficult to adjust and keep in adjustment. Consequently this method has not found favor and has been discarded for at least twenty years. The Bureau of Standards uses the Wheatstone bridge and reversing commutator method almost exclusively. The Thomson bridge method is capable of equal accuracy, but is much less convenient. The Smith difference method is not used in this country, but is favored in England. In both the Wheatstone bridge method as used at the Bureau of Standards and the Smith difference method, two resistance readings are necessary with a change in certain connections intervening which results in an elimination of the effect of the lead resistances. The average of the two readings of the measured resistance represents the resistance of the platinum coil. The changes in connections involve a number of contacts in the bridge network which are broken and made again to give a different bridge arrangement between the two readings. The contacts are made by heavy copper links dipping into mercury cups and have been shown to be of satisfactory constancy and reproducibility.

The Smith difference bridge and method were described in 1912.[78] Readings of thermometer resistance may be made directly to 0.00001 ohm, but the construction of the lower valued decades, from 0.001 to 0.00001 ohm is such as to place the limit of precision at ± 0.0004 ohm equivalent to $\pm 0.004^{\circ}$. The latest Bureau of Standards bridge, commonly referred to as the Mueller bridge,[59,85] permits readings directly to 0.0001 ohm and the degree of precision is undoubtedly very close to that figure. The Mueller bridge is probably the most accurate bridge of its kind ever devised.

The Mueller bridge permits temperature readings directly to 0.001° since in the most accurate thermometers a change of 0.0001 ohm is equivalent to 0.001° temperature change. Readings to any higher degree of precision must necessarily be made by a galvanometer deflection method. A number of objections may be raised to this scheme however. About 0.010 ampere is usually passed through the thermometer in order to realize sufficient sensitivity. This current generates heat faster than it can be dissipated with the result that the thermometer temperature increases until finally a steady state is realized. This increase may amount to 0.020°. The amount of temperature increase is governed by the specific heat, the heat conductivity and the degree of agitation of the medium in which

the thermometer is immersed. In order to use the deflection method, the steady state must be realized for each bridge setting. Consequently an accurate knowledge must be had of the temperature rise of the thermometer for each particular case. In most situations met with in practice, such information is not available and can only be obtained with considerable experimental difficulty. A second objection to the deflection method is the amount of time involved in making the readings. The temperature under investigation may change appreciably during the course of the readings and hence the desired precision would not be attained. Thirdly, the use of the deflection method presupposes constancy of lead resistances while making the deflection readings. This is not justifiable to the limit of precision involved, considering the amount of time which would be involved in making the readings. Furthermore, it is possible that under certain conditions the amount of heat dissipated by the thermometer due to the passage of current might be sufficient to raise the temperature of the system under examination. In view of these objections it is evident that the galvanometer deflection method is unsuited for temperature readings of an accuracy greater than $\pm 0.001^{\circ}$ using the Mueller bridge.

In order to measure the temperature of the oil bath and its fluctuations to less than 0.001° some other system of measurement must be employed. The bridge described below was designed to make this possible. Although the device has certain disadvantages which will be pointed out, it is capable of measuring temperature differences to 0.0002°. It must be borne in mind that to attain such a degree of sensitivity it may be necessary to sacrifice some convenience in measurements.

The Thermometer Bridge.

Design and construction.

In order to measure temperature changes in the thermostate of less than 0.001° and at the same time to determine the actual temperature with an accuracy as nearly comparable as possible, a special bridge was designed. It was constructed by the Leeds and Northrup Company and was built especially for use with their precision calorimetric thermometer. The bridge is basically of the ordinary, direct current, Wheatstone type. To obtain the necessary precision, the range of the bridge was correspondingly reduced. To permit calibration of the thermometer at the fixed points and use at the chosen temperature of 25°C., a series of fixed resistance coils were provided so that the small range of variation available could be applied in the neighborhood of the temperatures 0°, 25°, 32° and 100°C. Two guiding principles were followed in the design; the number of measuring resistance coils and the number of movable contacts in the bridge proper were to be kept at a minimum. The fewer the coils, the smaller the accumulation of errors resulting from the calibration of those coils. The fewer the number of contacts, the smaller the uncertainty due to variations in contact resistances.

The initial considerations in the theory of the bridge design may be considered with reference to Figure 1, which represents the fundamentals of the Wheatstone bridge. Let A represent the thermometer, B, C and D denote variable resistances, G a galvanometer and S a battery. The current which may be passed through A is limited by the heating effect on the platinum coil. If a given current is maintained through A, the deflection of the galvanometer for a given change in the resistance of A when the bridge is at balance, will tend to increase, the smaller the value of D and the larger the values of C and B. Such changes will necessarily be accompanied by an increase in the current through C and D if the current in A is kept constant. This would result in an increase in the power expenditures in B, C and D. In selecting the values of B, C and D it is desirable to use those which will give a maximum sensitivity in the measurement of A, but at the same time excessive power expenditures must be avoided in the coils in order that their resistances may remain fixed.

The thermometer used has an average resistance between 0° and 100° of 30 ohms. The most sensitive galvanometer at hand for this bridge has a coil of 45 ohms resistance and requires 250 ohms external critical damping resistance. On these bases it was calculated that if D was equal to 3 ohms, C equal to 30 ohms and consequently B equal to 300 ohms, the sensitivity would be twice that obtained if A, B, C and D were all equal to 30 ohms provided the same current passed through A. However, the power expenditure in C and D under the first set of conditions would be far in excess of the tolerated values with a current of 0.010 ampere through the thermometer. Since such a degree of unsymmetry in the bridge would only double the sensitivity, it was decided to design the bridge with

approximately equal arms. Under these conditions no excessive power expenditures are experienced with a thermometer current of 0.010 ampere. In order to use fixed coils in B, C and D and still be able to measure a range of resistance values for A, a slide wire was interposed between D and C. A low resistance was shunted across its terminals to increase the sensitivity. This reduced its effective resistance from 7.0 to 0.2 ohms. With this system the total measurable temperature range varies from 3.51° at 0° to 4.84° at 99.1°. The actual ranges of temperature covered by this equipment are -1.75° to 1.75°, 23.08° to 26.92°, 30.41° to 34.35° and 96.68° to 101.52°.

The final arrangement of this bridge is shown schematically in Figure 16. The galvanometer remains connected during measurements and the current is controlled with the tapping key, K. The symbol S denotes a switch and R denotes a resistance. Items S_3, S_4, S_5, R_s and R_d are all mounted on a bakelite panel and immersed in oil. They are the same pieces that were used in the potentiometer and resistance box calibration but the wiring arrangement has been altered as a comparison with Figure 12 indicates. With S_3 closed in position ①, the galvanometer sensitivity may be varied by adjusting R_s which is a resistance of 20000 ohms. With S_3 in position ②, R_s is effectively removed and R_d is adjusted for critical damping. The galvanometer is the same as used in the potentiometric calibrations of the alternating current bridge resistances described in a preceding section. In order to improve the sensitivity the distance from mirror to scale was increased from 3.1 meters, the distance used in those calibrations to 5.9 meters. The galvanometer is thermally insulated.

Figure 17 is a photograph of the bridge and potentiometer assembly. The mountings at the side of the bridge box were so placed as to permit nearly complete oil immersion of the various coils. The ratio coils (R_1) and (R_2) are wound on the same spool and hermetically sealed in oil in the container at the center of the side of the box. The slide wire, w, is visible on top of the box and its shunt R_5 is mounted beneath the panel. Coils for arms (R_3) and (T) are hung in the bath from the supports as shown.

Consideration of the temperature coefficient of the manganin wire of the coils indicated that in order to obtain a precision of three parts per million or better, which figure corresponds to 0.001° in thermometer temperature, temperature control of the main bridge coils to at least ±0.05° is necessary. Since the effective resistance of the shunted slide wire is only 0.2 ohm, a greater percentage variation in its resistance may be tolerated. Oil immersion of the shunt and slide wire is unnecessary because the room temperature is controlled to ±0.3° which is adequate.

Since control of the coils to ±0.05° is ample, the construction of the bath for this purpose is not as involved as with the thermostat for the conductivity cells.

The thermostat used for this work is shown in Figure 17 with the bridge in place. The tank of sheet copper is supported by an uninsulated wooden framework. A coil of copper tubing using tap water serves as the cooling unit and two Cenco knife blade heaters as the heating unit. These were controlled by a deKhotinsky thermoregulator acting through a vacuum tube assembly with a Cenco Relay. About 30 milliamperes are required for the relay so a vacuum tube with high plate current is required. The '45 tube of the power amplifier type is satisfactory. The wiring diagram is shown in Figure 18. It was found that the bath could readily be maintained at 25.00° ± 0.03° which is ample for temperature measurements to ±0.0002° using the resistance thermometer.

After the Cenco Relay had been in operation for a year and a half, trouble was experienced with sticking and burning of the contacts controlling the current for the heaters. All attempts at remedying the situation proved ineffectual so the relay was replaced by a Thyratron or mercury vapor tube. The electrical circuit is shown in Figure 19. The device functions perfectly and the temperature of the bath is still maintained at 25.00° ± 0.03°.

The bridge was designed so that the thermometer resistance would be determined by first measuring the coil plus the leads, then measuring the leads alone and by subtraction obtaining the resistance of the coil. A consideration of the four terminal thermometer, Figure 15, indicates the measurements necessary. It is evident that (c + coil + t) and (C + coil + T) may be measured. The sum of these two results is equal to (c + t + C + T + 2·coil). Also, (C + c) and (T + t) may be measured. The sum of these last two results will be equal to (c + t + C + T) so that the value of the coil resistance may be readily obtained. The measurements of (c + coil + t) and (C + coil + T) are made by connecting the thermometer at terminals 1 and 3 of the

bridge shown in Figure 16. The measurements of (C + c) and (T + t) are made by connecting the leads at terminals 1 and 2 and inserting a coil of known resistance between terminals 2 and 3.

In determining the thermometer resistance at each fixed point and at 25°, a separate coil is required in arm (R_3). In order to bring the balance point near the center of the slide wire in each case, the value of the (R_3) coils must be approximately equal to the average of the resistances of (c + coil + t) and (C + coil + T) for the temperature in question. A selection of the fixed thermometric calibration points was necessary before the values of the resistances could be estimated and, hence, before the values of the (R_3) coils could be chosen. The ice point, 0.000°C. and the steam point, which averages about 99.1°C. in this locality, were necessarily to be used. Unfortunately the calorimetric type thermometer cannot safely be used at the sulfur point because of distortion and resultant permanent resistance changes in the thermometer coil. Therefore the third fixed point chosen was the sodium sulfate transition temperature, 32.38°C. A preliminary approximate determination of the values of (c + coil + t) and (C + coil + T) was made by the Leeds and Northrup Company for the three fixed points and at 25°. From the data the necessary values for the (R_3) coils were calculated and included in the specifications of the bridge. The coils were constructed according to the Bureau of Standards pattern for standard resistances.

In order to realize the highest accuracy in the temperature measurements, a substitution method is used in the resistance determinations. For that purpose four more coils were required and are designated as the (T) coils. The values for these (T) coils were selected so that when a given (T) coil is placed in arm (T) of the bridge and the corresponding (R_3) coil in arm (R_3), the balance point may be brought on the slide wire by shunting the (T) coil with a relatively high resistance. The values for the (T) coils were chosen so that the balance would shift from one end of the slide wire to the other when the shunt was varied from about 2000 ohms to 20000 ohms. The effect of uncertainties in contact resistances in the shunt is rendered negligible by the use of such high shunting resistances in comparison with the (T) coils which range from 25 to 35 ohms. If the resistances of the parallel combinations in the (T) arm are known, then each setting of the slide wire for a given (R_3) coil corresponds to a known resistance in the (T) arm. Therefore if the thermometer is substituted for the parallel combinations and the balance point on the slide wire is determined, reference to the calibration data indicates the total resistance between the thermometer terminals which are connected. The accurate determination of the resistances of the parallel combinations will be described later. By the use of this method of measurement a knowledge of the exact resistances in arms (R_1), (R_2), (R_3) or the shunted slide wire is unnecessary. The final step in the design of the bridge was to select the value of the coil to be used in the measurements of the thermometer lead resistance. This is designated as the L coil. In order to select a single value which would be used for the measurements at all the temperatures, the Leeds and Northrup Company determined the values of (T + t) and (C + c) at 0° and 99.1°. If one of the (R_3) coils is put in arm (R_3) and the appropriate value of L has been selected, it becomes possible to balance (T + t + L) or (C + c + L) when placed in arm (T). The value of the L coil was chosen as the difference of the average value for the lead resistances at the two temperatures and the value of the (R_3) coil for 32.384° for use in arm (R_3). The result thus obtained for the L coil was 28.722 ohms.

Data regarding the thermometer bridge coils are found in Table 15. The specified coil resistances are tabulated in the second column of this table. The Leeds and Northrup Company carefully aged the coils and adjusted their values to within 0.002% of the specified values on the basis of their standard resistance coils. This care in preparing the coils insured that in every measurement to be made with the bridge, the balance point would lie on the slide wire. The values which the Leeds and Northrup Company found in terms of their standards are given in the third column of Table 15 and show excellent agreement with the specified values. The fourth and fifth columns contain values obtained by the calibration described below.

The calibration of the thermometer bridge coils.

As pointed out earlier, the Bureau of Standards was consulted regarding the measurement of the true temperature of the conductivity bath. A quotation from their reply follows: "The specifications for the International temperature scale...define temperatures between 0° and 660°C. in terms of the resistance of platinum, by use of the equation

$$\frac{R_t}{R_0} = 1 + At + Bt^2$$

when R_t is the resistance of a platinum resistance thermometer at temperature t, R_0 its resistance at 0°, and A and B are constants to be determined by calibration at the steam point and the sulfur boiling point. It is apparent that this equation involves only the ratio of resistances. This corresponds to the well known fact that in resistance thermometry it is not necessary to calibrate the resistances in terms of any standard since it is necessary to know only relative values. ...the accuracy of your temperature measurements ...depends on the accuracy with which you are able to determine the resistances of several coils in terms of the resistance of any one of them."

In order to make temperature measurements at 25° with an assured accuracy greater than ±0.001° it is therefore necessary that the T-coils and the L-coil inserted in arm (T) of the bridge be known in terms of an arbitrary standard to ±0.0001% and the thermometer calibrated at three fixed points with this bridge. The arbitrary standard of resistance selected was the 100-ohm Bureau of Standards coil which will be designated as R_s. This was certified in March 1934 to have a value of 99.999 International Ohms at 25° with an accuracy of ±0.005%. Since, however, only relative values were required its value was assumed to be 99.99900 units of resistance.

The comparison of the four T-coils and the L-coil with R_s necessitated the use of a number of combinations which included in addition the (R_s) coils. While a large number of combinations are possible, care was taken to select for use those permitting maximum precision in the final values. These combinations are shown diagramatically in Figure 20. In each case two arrangements are shown. One arrangement was placed in the (R_s) and the other in the (T) arm of the bridge and the balance obtained. They were then interchanged and the new balance point found. The high resistance shunt R_h was adjusted until no shift in the balance point was obtained upon interchanging, indicating that the two combinations were of equal resistance.

In every case the current to the bridge was about thirteen milliamperes and sensitivity of setting of the slide wire was about ±0.06 divisions representing about ±0.00002 ohm in arm T or ±0.0002° in thermometer temperature. The fractional parts of a division are obtained with a vernier arrangement giving readings to 0.02 division. This sensitivity means that the bridge is sufficiently sensitive to detect a change in temperature of ±0.0002°. The precision of any resistance determination as found by taking various combinations apart, assembling again and redetermining the balance point is about ±0.10 division. This corresponds to about ±0.0003° in thermometer temperature.

The various combinations were made using a stand constructed for the purpose and patterned after a type used at the Bureau of Standards in precise comparisons of standard resistance coils.[71] This stand with some coils in place is shown in Figure 21. Connection from the stand to the bridge is made by the two short links. These were found to have a total resistance of 0.00016 ohm. A third and longer link is needed in combination (f) of Figure 20 and it was found to have a resistance of 0.00008 ohms. Direct test showed that the heavy copper blocks of the stand have negligible resistance. The coils are connected together electrically by these blocks. The contacts are made by forcibly pressing the ends of the arms of the resistance coils into the holes of the stand or the straps on the bridge using screw collars. The holes and the ends of the coils are well amalgamated and repeated tests showed no variation beyond the limits of precision of bridge measurements, namely ±0.00003 ohm. The shunting resistance boxes were connected to the proper coil by means of two heavy insulated copper wires. The heavy copper leads were found by potentiometric measurements to have resistances of 0.002 ohms. This is negligible in comparison with the accuracy of 0.2 ohm needed for even the smallest shunt. A preliminary calculation indicated that these shunts would need to be known to only five significant figures. The shunts used here are the same two decade boxes used in the measuring arm of the alternating current bridge described earlier. They had been calibrated against the Bureau of

Standards coils and were reliable to ±0.003% for coils of 1000 ohms or less and to ±0.005% for coils of 10000 ohms. In every instance, therefore, the values were definitely known to five significant figures. The smallest shunt was about 2500 ohms and the largest was about 53000 ohms.

Two series of calibrations of the bridge coils were carried out, the first in May 1934 and the second in January 1935. In the first case only the large five dial box was used as a shunt, fractions of ohms being found from the shift in balance point of the slide wire for settings on either side of the resistance which, if it had been used, would have caused no shift in the slide wire setting. In the second case the two boxes were used in series and the setting could be brought as exactly to the center of the slide as the limit of precision would permit. Variations in contact resistances of these boxes had no detectable influence on the balance point. Such a result would be predictable considering the large values of the box resistances in comparison with the values of the coils being shunted and the relatively small variations in resistance observable in good, clean contacts.

Treatment of results.

From the measurements of the various combinations described above, it is possible to compute, by the solution of sets of simultaneous equations, the resistances of the individual coils. As a check on the method of calibration, the value for the resistance of coil R_4 was determined by two independent sets of measurements; these gave identical values (36.45236) which would be expected if the claimed precision of measurement was fulfilled. The entire calibration was repeated one year later. The detailed treatment of the results of the second series is described below.

The effective resistance of combination (a), Figure 20, is represented by X, then

$$\frac{1}{X} = \frac{1}{R_s} + \frac{1}{R_h}$$

or $$\frac{1}{X} = \frac{1}{99.99900} + \frac{1}{52892}$$

so that $X = 99.81030$ units.

Then $T_1 + T_4 + R_4 = X$ - two short links = 99.81014 units

In combination (b)

$$T_1 = \frac{1}{\frac{1}{T_4} + \frac{1}{R_s} + \frac{1}{R_h}} + \text{two short links}$$

or $$\frac{1}{T_1 - 0.00016} = \frac{1}{T_4} + \frac{1}{99.99900} + \frac{1}{2478.73}$$

Likewise in combination (c)

$$T_1 = \frac{1}{\frac{1}{R_4} + \frac{1}{R_s} + \frac{1}{R_h}} + \text{two short links}$$

or $$\frac{1}{T_1 - 0.00016} = \frac{1}{R_4} + \frac{1}{99.99900} + \frac{1}{5858.46}$$

Three relations have thus been obtained involving R_4, T_1 and T_4. The simplest solution was found to be by approximation. Values were assigned to T_1 and then T_4 and R_4 calculated. The sum of the three then was compared with the measured sum, 99.81014 units, obtained in combination (a). The Leeds and Northrup value was first used for T_1, and then revised until the assumption $T_1 = 26.59324$ units was made. Then from combination (b)

$$\frac{1}{T_4} = 0.02720024, \quad \text{and} \quad T_4 = 36.76439 \text{ units}$$

and from combination (c)

$$\frac{1}{R_4} = 0.02743298, \quad \text{and} \quad R_4 = 36.45248 \text{ units}$$

The sum of the three values, $T_1 + T_4 + R_4 = 99.81011$ units as compared with 99.81014 units measured. It was next assumed that $T_1 = 26.59325$ units,

then $\frac{1}{T_4} = 0.02720022$, and $T_4 = 36.76441$ units

and $\frac{1}{R_4} = 0.02743296$, and $R_4 = 36.45250$ units.

The summation yields 99.81016 units which is slightly better agreement so these were taken as the best values of T_1, T_4 and R_4.

As a check on these measurements, T_4 and R_4 were compared in combination (d). Assuming the above value for T_4 makes possible a calculation of R_4.

$$\frac{1}{R_4} = \frac{1}{T_4} + \frac{1}{R_h}$$

or $$\frac{1}{R_4} = \frac{1}{36.76441} + \frac{1}{4296.66}$$

so that $R_4 = 36.45250$ units.

This checks the above value for R_4 to better than one part in three and one-half million. It is an independent measurement and may, therefore, be offered as proof that the method is accurate to ±0.0003% as claimed for the precision of the measurement. As mentioned a similar agreement was obtained in the other series of measurements.

Next R_1 was compared with T_1 in combination (e). In that case

$$\frac{1}{R_1} = \frac{1}{T_1} + \frac{1}{R_h}$$

or $$\frac{1}{R_1} = \frac{1}{26.59325} + \frac{1}{3315.98},$$

so that $R_1 = 26.38168$ units.

The effective resistance X of combination (f) is

$$\frac{1}{X} = \frac{1}{R_s} + \frac{1}{R_h}$$

or $$\frac{1}{X} = \frac{1}{99.99900} + \frac{1}{34704.3},$$

so that $X = 99.71168$ units.

Now the effective resistance is also expressed as

$$X = T_2 + L + R_1 + \frac{1}{\frac{1}{T_1} + \frac{1}{T_4}} + \text{three links},$$

or $99.71168 = T_2 + L + 26.38168 + 15.43121 + 0.00024$

so that $T_2 + L = 57.89855$ units.

The solution for T_2 and L requires two additional comparison measurements. In combination (g)

$$\frac{1}{R_2} = \frac{1}{T_2} + \frac{1}{R_h}$$

or $$\frac{1}{R_2} = \frac{1}{T_2} + \frac{1}{3589.82}.$$

In combination (h)

$$\frac{1}{L} = \frac{1}{R_2} + \frac{1}{R_h}$$

or $$\frac{1}{L} = \frac{1}{R_2} + \frac{1}{3826.04}.$$

A combination of these expressions for R_2, T_2 and L may be written as

$$\frac{1}{L} = \frac{1}{T_2} + \frac{1}{3589.82} + \frac{1}{3826.04}$$

This equation with the previous equation,

$$L + T_2 = 57.89855 \text{ units},$$

makes possible the determination of L and T_2. This is best accomplished by a series of approximations. The Leeds and Northrup value for T_2 was first used and then revised until the assumption that $T_2 = 29.17563$ units was made,

then $$\frac{1}{L} = 0.03481511$$

and $L = 28.72316$ units.

The sum $T_2 + L = 57.89879$ units as compared with 57.89855 units. It was next assumed that $T_2 = 29.17551$ units,

then $$\frac{1}{L} = 0.03481525$$

and $L = 28.72304$ units.

By summation $T_2 + L = 57.89855$ which is satisfactory agreement with the measured value so these values for L and T_2 were selected. The value of R_2 may also be calculated now from combination (g) as previously expressed and a result of 28.94030 units is obtained.

In combination (i) the effective resistance X is expressed as

$$X = \frac{1}{\frac{1}{T_1 + T_2 + L + R_1 + R_4} + \frac{1}{T_4}} + \text{two short links}$$

or $$X = \frac{1}{\frac{1}{147.32598} + \frac{1}{36.76441}} + 0.00016$$

or $X = 29.42224 + 0.00016 = 29.42240$ units.

Then $$\frac{1}{R_3} + \frac{1}{R_h} = \frac{1}{X}$$

or $$\frac{1}{R_3} = \frac{1}{29.42240} - \frac{1}{3251.77}$$

so that $R_3 = 29.69105$ units.

Finally in combination (j),

$$\frac{1}{R_3} = \frac{1}{T_3} + \frac{1}{R_h}$$

or $$\frac{1}{T_3} = \frac{1}{29.69105} + \frac{1}{3677.62}$$

so that $T_3 = 29.93271$ units.

The results of both independent series of measurements are given in the last two columns of Table 15. On the average the 1935 values are higher than the 1934 values by 0.00026%. This change may reasonably be attributed to an actual change in the 100-ohm standard of that same percentage or 0.00026 ohm. Since the differences between the various values in the two series are appreciable after this change is taken into consideration, it is evident that for precise work involving temperature

measurements to 0.001° or better, the coils must be intercompared at least once a year.

Since the resistance measurements on the thermometer are all based on the effective values of the parallel combinations placed in the (T) arm and the relative values of these combinations are known with sufficient accuracy in terms of the arbitrary standard, it is apparent that the absolute value of the 100-ohm arbitrary standard is not needed. The thermometer resistance will always be expressed in terms of the arbitrary unit whatever the temperature. The limiting factor as far as the resistance measurement is concerned becomes the precision of making the readings for the various combinations rather than the accuracy of any certification of the resistance coils by the Bureau of Standards.

The calibration of the slide wire.

In order to complete the calibration and render the bridge ready for temperature measurements, the relation between a variety of resistances in the (T) arm and the corresponding slide wire settings was needed for each of the four (R_3) coils. For this purpose the appropriate coils were inserted in the (R_3) and (T) arms and the five decade resistance box was connected across the (T) coil. Then by adjusting this high resistance shunt, the whole slide wire could be investigated.

To determine the magnitude of the interval in the calibration data in which linear interpolation can be used, calibration of a portion of the drum was carried out in very small steps. This was accomplished as follows: coils R_3 and T_3 were inserted and T_3 shunted by a resistance which was so varied in the range 2460 to 2480 ohms as to cover the slide wire in steps of about one division from a drum reading of 200 to one of 210 or 0.1 drum revolution. There are 100 divisions per revolution and 10 revolutions possible. The values in the (T) arm were then calculated from the two known values of each parallel combination and plotted against drum reading. A straight line was drawn from the point for drum reading 200 to the one for drum reading 210. All of the other points were within less than 0.1 divisions of this line, the maximum departure being 0.07 division. The precision of the slide setting, 0.1 division, was previously indicated to be satisfactory since it corresponds to only 0.0003° in thermometer temperature. The calibration interval was therefore selected as 10 divisions of the drum and at no time has there been any indication that such an interval is too large. Only those regions of the drum were calibrated which gave promise on the basis of calculations of being useful in the present work. For coil R_1 in arm (R_3) which is the one used to make temperature readings at 0°, this extended from drum readings 400 to 450 and from 540 to 590. For coil R_2 in arm (R_3) used for readings at 25°, a wider range was measured, namely from division 300 to division 700. Similarly for R_3 which is used for readings at 32.38° and in the determination of lead resistances, drum readings 200 to 800 were calibrated. For R_4 or readings at the steam point the entire slide was calibrated.

The results for the slide wire calibration, which included two hundred twenty five points, appear in Table 16. In this table are given for each of the four coils used in the (R_3) arm, i.e., for each of the four working ranges of the bridge, the reading of the slide wire and the corresponding resistance in the thermometer or (T) arm of the bridge. In the computation of the effective resistance of the parallel combination of the T-coil and shunting box, the calibration corrections previously determined for the latter were applied. The precision of measurement of these resistance values is the same as for the calibration of the T- and L- coils and corresponds to 0.0003° in thermometer temperature.

Conclusion.

A precision Wheatstone bridge has been designed, built, tested and calibrated and found to be capable of making readings which are both accurate and precise to ±0.00003 resistance units in 30 units, which unit is the same as the International Ohm within ±0.005% based upon the Bureau of Standards certification. The bridge is applicable to measurements of temperature over limited ranges near 0°, 25°, 32.38° and 99.1° with a platinum resistance thermometer having a resistance at 0° of about 25 ohms. The absolute accuracy of such temperature measurements may be placed at ±0.0004° in so far as the measurement of thermometer resistance is involved.

The Calibration of the Resistance Thermometer.

Introduction.

Before the actual determination of the three fixed points used for the calibration of the thermometer is described, it is well to describe the actual manipulations

involved and to consider some of the disturbing factors which were encountered during the preliminary work. These included the effect of variation in room temperature on the lead resistance, of the heating effect of the measuring current on the thermometer resistance and the relation between these effects and the time required for the determination.

In making the measurements it was found that the L coil could be left in place while measuring the thermometer coil plus the leads without in any way affecting the balance point. The steps in measuring the thermometer resistance which may be followed with reference to Figure 16, involve the insertion of coil R_3 in arm (R_3), the connection of the thermometer leads to the terminals 1 and 2 of the bridge and the insertion of coil L between terminals 2 and 3. Then the balance points for (c + C + L) and for (t + T + L) are found with the necessary changes in contact connections made between the two readings. The coil for arm (R_3) for the temperature in question is inserted in place of coil R_3 and the thermometer lead connections are changed to terminals 1 and 3 in order to measure the platinum coil resistance. The balance points for (c + t + coil) and (C + T + coil) are found with the necessary contact changes intervening. Finally coil R_3 is replaced in arm (R_3) and the original thermometer lead measurements are repeated. Usually this complete procedure requires from eight to ten minutes. The major portion of the time is occupied in changing the connections. When the thermometer was first tested, excessive changes in lead resistance due to fluctuations in room temperature were found to occur in the time required for adjustment. These were minimized by covering the leads, which are wrapped together as a unit for most of their length, with two concentric pieces of rubber tubing. The calculations of thermometer resistance are based on the assumption that the room temperature changes are gradual so that the average of the measured (c + C) and (t + T) values represent with sufficient accuracy the actual lead values at the time the (c + t + coil) and (C + T + coil) readings are taken. The differences between the lead values before and after the coil readings amount to about 0.00005 ohm on the average with the leads thermally lagged. The error in assuming that the average lead values represent the actual lead values when the platinum coil is measured is negligible since under proper conditions it is not likely to exceed 0.00002 ohm which corresponds to 0.0002° in thermometer temperature. If a greater difference than 0.00005 ohm in the two lead resistance determinations is found, it is usually traceable to an increase or decrease in room temperature caused by a disturbance in the regulation due to incorrect adjustment of the rate of cooling the room air. For highly accurate temperature measurements such resistance readings are rejected because the uncertainty in the values of the lead resistances at the time of the coil measurements may introduce an error greater than might be tolerated. The concordance between the several sets of results obtained for each of the fixed point measurements serves to substantiate the assumption made regarding the values of the lead resistances. The data may be found in the following sections. If this assumption were in error, greater variations in the apparent platinum coil resistance would be expected at the fixed points than are actually found.

The length of time involved in making the readings and adjustments constitutes the most serious objection to this system of resistance thermometer measurement. If a commutating device could be developed which would permit rapid changes in the contacts and still maintain the constancy of their values, the total time for a complete reading could probably be reduced to three or four minutes. This would decrease the uncertainty in the determination of the lead resistances at the time of the platinum coil measurements. The use of a commutating device would also make the manipulations of temperature measurement appreciably simpler. The addition of such an accessory, however, would necessarily increase the number of movable contacts in the bridge network. From that point of view the present arrangement is superior. If it could be demonstrated that the additional contacts were sufficiently constant and reproducible, then their introduction would be justifiable.

In making the readings for (c + t + coil) and (C + T + coil) the balance point can readily be obtained by tapping the battery key and observing the direction of deflection. By adjusting the slide wire slightly and repeating the tapping, the exact balance point can readily be obtained. If the key is left closed, in a few seconds a deflection may be noted due to the heating of the thermometer coil by the current, even though this current may be only 0.006 ampere. The deflection is complete in about ten seconds. With larger currents the time is even shorter before deflection due to this cause is noted. After proficiency in manipulation of the bridge is acquired, it is possible to judge from the speed of the galvanometer deflection the approximate amount of slide setting adjustment needed and the final balance is quickly obtained. By this procedure one of the serious objections raised to the Mueller bridge method for highly precise readings is avoided, namely, the uncertainty in the temperature increase of the thermometer coil caused by the heat generated in the coil itself. In the method described herein

such temperature increase is eliminated.

Calibration at the ice point.

Introduction.

The ice point or the temperature at which ice and air saturated water are in equilibrium at a pressure of one standard atmosphere is a basic fixed point on the International Temperature Scale. It has been used for many years as a calibration point in thermometry. Extended investigations at the International Bureau of Weights and Measures[20,65] and at the Reichsanstalt[66] near the close of the last century resulted in the development of an empirical technique for reproducing the ice point. The method is fundamentally unsound for if the water of melting is not periodically drained off, the temperature readings rise. In a properly designed system, the temperature should be independent of the relative amounts of water and ice as long as both phases are present. Burgess[4] did not offer any suggestions regarding technique in presenting the recommendations of the General Conference of Weights and Measures of 1927 other than to state that "the temperature of melting ice is realized experimentally as the temperature at which pure, finely divided ice is in equilibrium with pure, air saturated water under standard atmospheric pressure." White[91] at the Geophysical Laboratory in Washington has made a careful study of the ice point and his procedure published in 1934 is based on a sound foundation. In this method finely shaved ice is placed in a closed vessel called the "cold cell." This is provided with glass tubes for adding and removing water and air and also with a well in the center for introduction of the thermometer. The filled cold cell is completely packed in crushed ice. According to White, even if relatively impure ice is used to fill the cold cell, the true ice point may be realized by repeated washing of the ice with air saturated water at a temperature of 0° so that melting is avoided. In this fashion the surface impurities are removed and, to quote from White, "the ice will become superficially as pure as the water it is washed with, so that this water alone will determine the temperature." The rate of diffusion of impurities from the body of the ice particles is sufficiently slow to prevent difficulties from that source. White indicated that mere washing of the ice is insufficient to realize the true ice point. It is essential that melting of the ice be avoided during the washing. By this method White successfully reproduced the ice point and was able to maintain constancy of 0.0001° for even as long as a day. The temperature variations were determined with thermocouples.

The technique of calibration at the ice point.

The White method has served as the basis of the present thermometer calibration. The cold cell consists of a flat bottom Pyrex tube 6 cm. in diameter and 21 cm. in height. This is closed by a clean rubber stopper with tubes inserted as shown in Figure 22. The thermometer is placed in the long 1.5 cm. test tube extending into the cold cell. The tube is filled with distilled water to aid in thermal contact between the contents of the cold cell and the thermometer. The water for washing the ice is kept in a one liter Florence flask. Both the cold cell and the Florence flask rest on small brass stands in an ordinary copper wash boiler fitted with a drain at the bottom and packed full of shaved ice. This tank is mounted in a wooden box with Sil-O-Cel insulation surrounding it. By proper manipulation of the stopcocks, pinch clamps and suction shown in Figure 22, air freed from CO_2 can be drawn through the flask to saturate the water. The water can be forced into or removed from the cold cell. All of the tubing near the cold cell and the flask is completely covered with ice to cool the water and air going into the flask or cold cell.

The procedure followed in making a determination is to fill the flask with water which has a conductivity of from 0.4 to $0.7 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25°. This is then put in place in the tank and shaved ice packed around it. Two or three days are allowed to chill the water and to saturate it with air which is drawn through at intervals. During this period it is necessary to replenish the ice every eight to ten hours. Clear pieces of commercial crushed ice supplied to the Chemistry Department are then selected, washed with distilled water and shaved. The cold cell is packed as full as possible, the stopper inserted and the thermometer, which has been previously chilled in a mixture of ice and

water, is put in place. Shaved ice is heaped around the cold cell so that it is completely surrounded by ice as shown in Figure 23. Readings of thermometer resistance taken as soon as possible indicate a rapid attainment of equilibrium. Chilled water is added and removed according to the suggestion of White until an essentially constant resistance is obtained. This condition was generally realized after two washings and was accompanied by a temperature rise of about 0.003°. Four or five washings were made in each of the four completely successful runs obtained. Readings may be taken as long as desired, the ice packing being replenished as needed. In two cases readings were satisfactorily checked after the apparatus had been set up over night.

The shaving of the ice is accomplished by means of the device shown in Figure 24. A box with no bottom and containing pieces of crushed ice is drawn back and forth through the brass lined channel. In the center of the bottom of the channel there is a slot at right angles to the direction of movement of the box. A steel knife clamped in this slot serves to shave off the ice which is collected in a pan beneath the slot. (A similar device was used by Pernet[66] at the Reichsanstalt in 1894 so that no originality of design is claimed.) The electrical drive facilitates the operation as, on the average, forty liters of crushed ice are used per day while runs are in progress.

Results of the ice point determinations.

The resistances as measured in the four satisfactory runs are tabulated in Table 17. It may be observed that the presence or absence of the wash water produced no systematic variations in temperature. A film of liquid remains on the ice particles when the wash water is removed; if the wash water is air-saturated no change in the temperature should result since the equilibrium temperature would not be changed. Moreover the film of liquid left on the ice must quickly become air-saturated if it is not already so. Since no systematic variation in the temperature of the system was observed the wash water must have been air-saturated. White[91] suggested this constancy of temperature as a criterion of completeness of air saturation.

The ice used in the cold cell in runs 3 and 6 was clear, selected pieces of commercial ice. That for run 4 was made in an electric refrigerator using conductivity water although no special precautions were taken to keep the sample out of contact with the atmosphere during solidification. The cubes obtained had a considerable quantity of entrapped air and a slight odor from the foodstuffs which had been in the refrigerator. The ice for run 5 was made by freezing conductivity water in two one liter electrolytic beakers using a mixture of ice and salt. This product was very clear and since all the water did not freeze, there was very little entrapped air. The water from the melted commercial ice had a conductivity of $22.0 \cdot 10^{-6}$ohm^{-1}cm.$^{-1}$ at 25° whereas that from run 4 had a conductivity of $2.3 \cdot 10^{-6}$ohm^{-1}cm.$^{-1}$ and from run 5 of $2.8 \cdot 10^{-6}$ohm^{-1}cm.$^{-1}$ both at 25°. For all of these samples the melting point of the ice on the basis of contaminating electrolyte would be higher than -0.001°. However, when adequate washing was employed no variation in the ice point resistances which could be attributed to impurity was found. Several samples of the first and second wash waters were tested after removal from the ice and had conductivities of about $6 \cdot 10^{-6}$ohm^{-1}cm.$^{-1}$ at 25° which represented depressions of the ice point of about 0.0002° as compared with nearly 0.001° for some of the ice samples. These results are in accord with the results obtained by the resistance measurements which show an early realization of constant temperature and also with the statement of White[91] concerning the influence of impurities in the ice used. Between runs 5 and 6, the thermometer was maintained at the steam point for six hours to ascertain if such treatment might affect the ice point resistance. The results indicate no appreciable change in resistance.

Since an increase in pressure of one atmosphere lowers the ice point by 0.007°, slight pressure corrections were necessary. The barometric readings ranged from 730 to 750 mm. during these runs so that corrections of from -0.0002° to -0.0003° were required.

The values selected for use in computation of the thermometer resistance are those for each run following the asterisks in Table 17. The remainder of the readings can be rejected on the grounds that they were obtained under conditions which did not represent the true ice point. Considering only the values obtained after the desired conditions were realized, it may be observed that the maximum variation between readings in individual runs is 0.00013 unit corresponding to a temperature difference of 0.0013°. The average deviation from the mean ranges from ±0.00001 to ±0.00003 unit which corresponds to ±0.0001° to ±0.0003°. The respective average resistances for the four runs when corrected for the effect of pressure on the ice point are 25.50570, 25.50568, 25.50565 and 25.50571 units. The average

value of these four is 25.50569 units and the average deviation from it is ±0.00002 units which corresponds to a temperature variation of ±0.0002°. Taking into account the uncertainties in bridge calibration as well as the observed variations in measured resistances, the resistance of the thermometer at 0.000° may be expressed as 25.50569 ±0.00004 units. This value has undoubtedly changed in the meantime since these measurements were carried out in February and March of 1935, but the nature of the results indicates the accuracy which may be realized in such a determination with the equipment and precautions used.

Calibration at the sodium sulfate point.

Introduction.

The first careful determinations of the temperature of transition of sodium sulfate decahydrate to anhydrous salt were made by Richards[67] in 1898 and by Richards and Wells[70] in 1903. They demonstrated that purification by recrystallization from water of either a commercial product or samples prepared in the laboratory by the interaction of $NaHCO_3$ and H_2SO_4 produced a salt with a definite transition temperature. Successive recrystallizations resulted in a gradual increase in the transition temperature until a value constant to ±0.001° was obtained. They found that in realizing the transition temperature, the most satisfactory results were obtained by slowly melting the hydrated salt. The reverse process was deemed unfavorable because of the tendency of the hydrate to form a supersaturated solution and the relatively slow rate at which the anhydrous form dissolves. The temperatures were measured with a number of mercurial thermometers. Richards and Wells claimed that they had determined the transition temperature as 32.383° ± 0.001° on the Hydrogen Scale. In the light of the statement from the Bureau of Standards quoted on page 8 relative to the limitations of mercury thermometers it is unlikely that such a degree of accuracy was realized. The uncertainty should more properly be placed nearer to ±0.002° or even ±0.003°.

Richards and Wells compared the methods of realizing the ice, steam and sodium sulfate points and came to the conclusion that this last transition temperature was probably the most useful of the three. Since that time the technique for realizing all three points has been improved, but the ice and steam points have profited to a much greater extent. It is doubtful therefore if the sodium sulfate point is more useful than the other two at the present time.

Dickinson and Mueller[10] reexamined the sodium sulfate point in 1907 while making an extended study of calorimetric type resistance thermometers at the Bureau of Standards. Two such thermometers were calibrated at the ice and steam points and the complete evaluation of the thermometer constants obtained by a series of comparisons in a water bath with eight mercurial thermometers at 30°, 40°, 50°, 60° and 70°. From the results obtained, Dickinson and Mueller concluded that the platinum resistance thermometers could be used as interpolating devices for the International Hydrogen Scale of Temperature to within 0.002° or 0.003° in the interval 0° to 100°. These two platinum resistance thermometers were then used for the transition temperature determination. The procedure of Richard and Wells was modified slightly. The hydrated salt was partially melted and recrystallization then started by cooling the tube in water. Dickinson and Mueller varied the temperature of the water bath in which was placed the assembled tube of salt and thermometer all enclosed in a brass shell. Changes of ±10° from 32° produced changes in the temperatures indicated by the resistance thermometers of only a few thousandths of a degree while with the water bath at 32° or 33°, no greater variations than 0.0005° were observed. A careful study of the effect of impurities on the transition temperature was also made. In general the presence of ±0.001% of other salts lowers the temperature of transition by 0.001°. The final results were obtained with samples subjected to numerous recrystallizations using a commercial product and also a material prepared at the Bureau by the interaction of Na_2CO_3 and H_2SO_4. Variations in mean values of as much as 0.003° were observed for different samples. The value finally selected by them as being the most accurate was 32.384° on the International Hydrogen Scale.

The International Hydrogen Scale adopted in 1887 and based on the constant volume hydrogen thermometer, served as the fundamental practical scale before the introduction of the International Temperature Scale in 1927. A number of careful investigations demonstrated that this scale

does not accurately reproduce the Thermodynamic Centigrade Scale over the entire range. Buckingham[3] at the Bureau of Standards presented a careful analysis of the subject in 1907. For temperatures near 30°, the results of his studies and those of other investigators indicate that the International Hydrogen Scale is too high. The differences vary depending on the method of attack on the problem but the average is about 0.002°. Consequently the value of 32.384° which Dickinson and Mueller obtained and the value of 32.383° which Richards and Wells obtained for the transition temperature when considered with reference to the present International Centigrade Scale, are too high by about 0.002°. It was probably as a result of such considerations that the International Committee in 1927 expressed the value for the sodium sulphate point as 32.38° on the International Temperature Scale even though the results of two careful and independent determinations checked to 0.001° on the International Hydrogen Scale.

A redetermination of this transition point on the basis of the International Temperature Scale would be highly desirable in view of the agreement which has been obtained in earlier determinations and the general utility of such a fixed point. Undoubtedly a careful determination or series of determinations would serve to render it as basic a fixed point as the sulfur point for example.

The continued use of the value 32.384° rather than 32.38° may be partially justified on the basis of work done at the Rockefeller Institute of Medical Research. Dr. D. A. MacInnes, the Director of Physico-Chemical Research at the Institute, in conversation and correspondence has pointed out that his aid, Dr. T. Shedlovsky, recently calibrated a strain free thermometer at the ice, steam and sulfur points. Using this thermometer he measured the sodium sulfate point and obtained 32.384°. This result is expressed as a temperature on the International Temperature Scale rather than on the International Hydrogen Scale.

Purification of materials.

Three samples of $Na_2SO_4 \cdot 10H_2O$ were prepared. Samples A and B were derived from J. T. Baker C. P. $Na_2SO_4 \cdot 10H_2O$. The raw materials for Sample C were J. T. Baker C. P. anhydrous Na_2CO_3 and Baker and Adamson C. P. H_2SO_4.

Sample A was recrystallized four times from conductivity water in Pyrex vessels, in each case the solution being nearly saturated at 32°. The starting material was dissolved in water at room temperature and filtered through a hard filter paper in a porcelain Büchner funnel to remove foreign matter. The filtrate was evaporated until the solution was nearly saturated at 32°. After cooling the solution with a mixture of ice and salt, crystallization was induced by seeding with a small crystal from the preceding step in the process. Vigorous stirring during the crystallization coupled with marked supercooling resulted in the production of fine crystals. These were separated from the mother liquor by centrifuging in platinum cups. After drainage the salt was washed twice by making a sludge with conductivity water, centrifuging and then repeating the process. Before the fourth crystallization this process was repeated, but a clean porcelain filtering crucible was used instead of the Büchner funnel. A very slight amount of lint was acquired by the salt in the early stages of purification. One hundred forty-one grams of clear hydrated salt were finally obtained from one thousand grams of starting material.

Sample B was treated in similar fashion, but five recrystallizations were employed instead of four. One hundred sixty six grams of product were obtained from one thousand sixty seven grams of starting materials.

In the preparation of Sample C one thousand grams of the Na_2CO_3 were subjected to two successive crystallizations as $Na_2CO_3 \cdot 10H_2O$. The salt was first dissolved in water and filtered through a Büchner funnel using a hard filter paper. A much greater quantity of foreign matter was contained in this material than was found in the C. P. $Na_2SO_4 \cdot 10H_2O$. The filtrate was evaporated until nearly saturated at 35°, then cooled with an ice-salt mixture, vigorously stirred and seeded with a crystal of C. P. $Na_2CO_3 \cdot 10H_2O$. The product was separated from the mother liquor by centrifuging. The second crystallization from a solution again approximately saturated at 35° yielded about one thousand ninety grams of decahydrate of good appearance. One thousand grams of this product in solution were then treated with a slight excess of the H_2SO_4 which has been redistilled in an all glass apparatus, the middle fraction only being used for this purpose. After the H_2SO_4 was added to the Na_2CO_3 solution, the CO_2 was removed by boiling and water was then slowly evaporated until the solution was nearly saturated at 32°. The $Na_2SO_4 \cdot 10H_2O$ was crystallized out, centrifuged and washed twice as for samples A and B. This material was recrystallized four times in

manner similar to that used for sample A. A final yield of one hundred twenty-two grams of hydrated salt was obtained.

Qualitative analytical tests were not performed on these samples. Richards and Wells[70] and Dickinson and Mueller[10] indicated that the order of agreement between transition temperatures for various samples serves as a satisfactory criterion of purity of materials. Dilute aqueous solutions of all three samples had a pH of about six when measured with chlor phenol red and brom thymol blue as indicators. No attempt was made to measure the pH at definite concentrations. However, the results serve to indicate that sample C was essentially freed of the excess H_2SO_4 used in its preparation.

The technique of calibration at the sodium sulfate point.

The apparatus used was patterned, with a few slight structural modifications, after the type used by Dickinson and Mueller. The tube for holding the salt may be faintly seen in the foreground of Figure 25. It is of pyrex glass with the dimensions as indicated in Figure 26. The long portion of the tube is deformed as shown in order to decrease the volume slightly. This was found essential when using sample C with only one hundred twenty-two grams of salt available. The salt was stirred with a ring nickel stirrer. The brass shell containing the tube, salt, stirrer and thermometer was placed upright and nearly submerged in a small circular water bath 24 cm. in diameter and 39 cm. in height. Mechanical stirring and electrical heating of the bath were provided, the latter being controlled by a magnetic relay so that the temperature of the bath could readily be maintained at about 32° within $\pm 0.1^\circ$.

Preliminary tests indicated that some additional care must be exercised in the procedure for reproducing the transition temperature over that recommended by Dickinson and Mueller. They suggested partially melting the salt in warm water and then initiating formation of the hydrate by running cold water over the tube. It was found that this method did not always produce the equilibrium temperature so the following procedure was adopted. The salt, containing some of the anhydrous form due to exposure to the air, was introduced into the glass tube and warmed in water at 40° or 45°. When the mass became sludge-like in character, it was removed and cooled under running water with stirring until a mercurial thermometer showed that the equilibrium temperature was approximately attained. Excessive warming or cooling usually failed to produce the desired results. This procedure is identical in principle with that of Dickinson and Mueller, but is somewhat more specific in details and more certain to give the desired results. When the transition temperature was attained, the tube was placed in the brass shell, the thermometer inserted, the cover put in place and the unit put into the water bath. The salt was stirred occasionally, but if the stirring was not vigorous, no detectable rise in temperature was noted. The resistance was determined at intervals for ten or twelve hours maintaining the water bath above and below 32.38° during this time.

Results of the sodium sulfate point determinations.

The thermometer resistance values are tabulated in Table 18 for the three samples. The time of measurement and the water bath temperature are also indicated. An inspection of the data shows that in no cases was a systematic difference observed in resistance whether the bath was adjusted for "melting" or "freezing." A change in resistance equivalent to a drop in temperature of about 0.001° is observable in the results for sample A coincident with the change in bath temperature. No explanation can be offered for this decrease in resistance. A comparison with the results for samples B and C indicates that possibly a slight contamination from some source had occurred. The average values for the three runs are 28.76964, 28.76962 and 28.76961 units. The values used in computing the averages are indicated by asterisks. The average deviations vary from ± 0.00002 to ± 0.00004 unit. The grand average of 28.76962 $\pm$ 0.00001 units may be selected then to represent the resistance of the thermometer at a temperature of 32.384° at the time of calibration, namely April 1935. The agreement between the various samples indicates that a temperature constant and reproducible to at least $\pm 0.0005^\circ$ was attained. This is a better agreement than Dickinson and Mueller realized; they found values ranging from 32.381° to 32.384° for the transition temperature. This difference of 0.003° corresponds to a difference of 0.00030 unit with the thermometer used in this work.

A number of preliminary measurements were made on C. P. $Na_2SO_4 \cdot 10H_2O$

subjected to one recrystallization to reduce the crystals to convenient size. These results when compared with the final value indicated a temperature 0.002° or 0.003° too low for the impure material.

It was found that with a steady current of 0.006 ampere passing through the thermometer the temperature of the platinum coil was increased by about 0.0020°. At the ice point the same current raised the temperature by 0.0035°. This serves as confirmation of one of the points raised in the discussion of the inapplicability of the Mueller bridge to measurements of an accuracy greater than 0.001°. Therein it was contended that the increase in temperature of the platinum coil is greatly dependent upon the physical characteristics and state of the medium in which the thermometer is placed. As pointed out earlier, the method used in the present work is free from this uncertainty resulting from changes in temperature of the platinum coil due to the flow of current.

Calibration at the steam point.

Introduction.

The work on the ice point at the International Bureau of Weights and Measures and at the Reichsanstalt near the close of the last century was accompanied by a thorough investigation of the steam point.[19,20,65,66,82] Apparatus in a variety of forms and of varying degrees of complexity was developed by Pernet, Chappius and others. Mueller and Sligh[60] in 1922 pointed out defects in these earlier instruments and offered the design of a superior device. They indicated that a number of conditions must be satisfied in a properly designed hypsometer. The space for the thermometer must be jacketed by steam. The steam bathing the thermometer must be free of superheat. An accurate means must be available for measuring the pressure in the steam space. Provisions must be made for securing constancy of pressure and temperature in the steam space. The contents of the hypsometer must be purified by a rapid and thorough removal of air from the steam.

In the earlier hypsometers, the steam was introduced at the bottom of the thermometer chamber so that it traveled upwards and at the top was directed down so as to jacket the incoming steam. It was necessary to make two pressure measurements in order to find the actual steam pressure. The barometric pressure was found by ordinary methods and a small water manometer served to indicate the excess of pressure over atmospheric pressure inside the device. A positive pressure was needed to circulate the steam and remove the air. Mueller and Sligh introduced the steam at the top and allowed it to flow downward in two parallel streams. To quote from their article, "This arrangement secures steam jacketing of the thermometer space, avoidance of superheat in the steam, since the boiler is located at a distance and ample cooling surface can be provided between the boiler and thermometer space, and eliminates entirely the necessity for a water manometer to measure the excess pressure of the steam. The density of the steam being less than that of air, a column of steam flowing downward in a pipe open to the air at the bottom is stable, while if the steam is flowing upward in a pipe, stability can only be attained by restricting the escape of steam sufficiently to cause the pressure in the pipe to exceed that of the atmosphere. The downward flow of the steam also greatly facilitates the removal of air from these spaces." This design is in accord with the recommendations of the General Conference of 1927 as presented by Burgess;[4] "The temperature of condensing water vapor is realized experimentally by the use of a hypsometer so constructed as to avoid superheat of the vapor around the thermometer, or contamination with air or other impurities. If the desired conditions have been attained, the observed temperature should be independent of the rate of heat supply to the boiler, except as this may affect the pressure within the hypsometer, and of the length of time the hypsometer has been in operation."

The instrument used by Mueller and Sligh was constructed of brass the inside being tinned. This is a disadvantage as it is impossible to tell the condition of the interior of the apparatus by visual inspection. The instrument was compared in operation with an older Chappius type hypsometer at the Bureau of Standards and the new instrument gave slightly more concordant results. However, to quote Mueller and Sligh again, "Fortuitous erros of about 0.005° persisted and are apparently due to irregular fluctuations in atmospheric

pressure or to errors in measurement of barometric pressure indicating that improvements in this respect will require the use of a closed system and better temperature control of the barometer." They did not indicate the uncertainty in the barometer temperature. It was found that the control of the room temperature to 0.3° eliminated that source of error in the present work.

The technique of calibration at the steam point.

An all Pyrex glass hypsometer designed according to the principles laid down by Mueller and Sligh was constructed for this determination. It is shown in Figure 27 enclosed in a box made of insulating board fastened to a metal framework. The steam is generated in the boiler at the bottom by means of an external electric heater. This is of chromel wire wound in a helical coil and then formed into a larger helix curved to fit the boiler and held in place by porcelain cement. The heating of the water is uniform and with a few pieces of quartz in the flask, steady ebullition is readily obtained. The steam proceeds upward through the narrow tube at the right where any superheat is removed. It enters the thermometer space tangentially to avoid direct impingement on the thermometer stem and then proceeds downward. The thermometer is held in place by a rubber stopper covered with tinfoil. The side arm shown at the left in the photograph is for venting of the air. The small water cooled condenser just above the boiler serves to convert the balance of the steam to liquid and return it to the boiler. Some steam is lost in operation at the side vent. Normally the hypsometer may operate for five to eight hours before it becomes necessary to replenish the water supply. Mueller and Sligh installed a reservoir to maintain a constant water level in the boiler. Such a device was not found necessary, but it could readily be added to this instrument if desired. Conductivity water is used as the source of the steam. To determine if the boiling point changed due to contamination from the glass, a sample with an initial conductivity of $0.7 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25° was boiled for eight hours in the hypsometer. At the end of that time its conductivity at 25° had increased to $2.2 \cdot 10^{-6} ohm^{-1} cm.^{-1}$. Another sample which had been boiled for at least 15 hours with occasional additions of fresh water and had been allowed to remain for more than a week in the hypsometer had a conductivity at 25° of $4.6 \cdot 10^{-6} ohm^{-1} cm.^{-1}$. The boiling point elevation of such solutions above the boiling point of pure water on the basis of dissolved electrolyte is negligible, being at most 0.0001°.

In practice, the heating current is varied to insure that the observed boiling point is independent of the rate of heat supply. No discordance of results was obtained when the input was changed from 230 watts which caused a slow venting of steam at the side arm to 410 watts which produced a relatively rapid discharge of steam at the vent. Further increases in power resulted in bumping of the water in the boiler and consequent fluctuations in temperature.

The boiling point of water is very dependent on the prevailing pressure. The General Conference of 1927 expressed this variation as

$$t_p = t_{760} + 0.0367(p-760) - 0.000023(p-760)^2$$

where p is the pressure in the hypsometer measured in millimeters of mercury and t_{760} is equal to 100.000°. The figure 760 corresponds to standard atmospheric pressure which is defined as the pressure due to a column of mercury 760 mm. high, having a mass of 13.5951 grams per $cm.^3$, subject to a gravitational acceleration of 980.665 cm. per $sec.^2$, and is equal to 1,013,250 dynes per $cm.^2$. The evaluation of p may therefore be secured by a mercury barometer at the same level and in the vicinity of the hypsometer. An examination of the above equation indicates that a change in pressure of 0.02 mm. serves to change the boiling point by approximately 0.001°. It is evident, therefore, that for a precise determination at the steam point, accurate barometric readings are needed. The best commercial barometers may be read to the nearest 0.05 mm., but are not reliable beyond $\pm$0.10 mm. Consequently the barometer described in the next section was designed and built in order to determine the barometric pressure to at least $\pm$0.02 mm.

Apparatus for the measurement of barometric pressure.

Introduction. The originator of precise barometric measurements was H. Wild[93] whose investigations at St. Petersburg in Russia during the last half of the 19th century are classical. The most accurate device for the measurement of atmospheric pressure is a "Normal Barometer." Wild defined this as "an instrument which permits the measurement of the pressure of the air...not only with great accuracy, but also absolutely independent of the special instrument used, in generally intelligible and reproducible units." He considered that the mercury barometer is best suited for use as a Normal Barometer. Marvin[56] has elaborated this definition by stating that "the construction (of a Normal Barometer), however, is such that those errors which cannot be wholly eliminated can yet be ascertained from the indications of the instrument itself." By virtue of their construction, the majority of mercury barometers cannot be Normal Barometers. For example, in the barometer with a fixed pointer at the lower limb, there is no available means for determination of the residual gas pressure in the vacuum space. This can be found only by comparison with an instrument in which the correction can be measured, that is to say, with a Normal Barometer.

A consideration of the work of Wild[93] and of Marek[52,53,55] at the International Bureau of Weights and Measures from 1881 to 1884 as well as the writings of Abbe[1] of the United States War Department in 1887 and of Marvin[56] of the United States Weather Bureau in 1912 indicated that an accuracy of ± 0.02 mm. or better can be attained only with a Normal Barometer. The instrument used in the present work was designed therefore on the basis of either reducing the various errors to negligible quantities or of providing for their measurement with the requisite degree of accuracy.

Description of the Barometer. The barometer assembly is shown in Figure 28, the upper and lower limbs in Figures 29 and 30 and a drawing to scale of the glass portions is given in Figure 31. The instrument is constructed of Pyrex glass with a Pyrex plunger to assist in changing the mercury levels. Certain portions in Figure 31 are indicated by dotted lines. These were necessary for the filling operations, but were removed when that was completed. After the glass had been cleaned with chromic acid solution and thoroughly rinsed with several changes of distilled water for a day, it was allowed to drain dry. It was then connected at a point a of Figure 31 to an evacuation system consisting of a mercury diffusion pump backed by a rotary oil pump. Tube b dipped into a dish of mercury which had been purified by the same method described in an earlier section dealing with the filling of the thermoregulator for the large thermostat. A liquid air trap was interposed between the diffusion pump and the barometer. The glass was flashed with a hand torch during the pumping for a half hour shortly after the evacuation was begun and then for three quarters of an hour after it had proceeded for five and one-half hours. The pumping was continued for eleven hours. Measurements with a McLeod gauge showed that the pressure was always less than 0.01 micron. The instrument was filled by raising the mercury level in b until the mercury flowed over into the large bulb. During this time the mercury was heated as it entered the barometer proper. When a sufficient quantity had been added, the vacuum was carefully released so that the entering air served to force the mercury into the upper part of the barometer and the dotted portions of Figure 31 were then cut away. The filled barometer was transferred to the constant temperature laboratory and finally mounted as shown in Figure 28. The standard is of nickel-plated iron with rubber lined, nickel-plated brass clamps for supporting the barometer at suitable points. The plunger visible in Figure 30 is operated by a rack and pinion device to permit gradual movements up or down. It was lowered until the mercury filled the upper limb and began to flow into bulb c of Figure 31 which may also be seen at the left in Figure 29. By quickly raising the plunger, the thread of mercury in the capillary was broken and a Torricellian vacuum was obtained in the upper space. Any gas which had been present was all forced into the bulb and entrapped there. This device was pictured by Abbe,[1] but not ascribed to anyone. Marek[52,53] used it with poor success, but in this case it functioned admirably.

The lower limb as seen in Figure 30 is protected by a dust cap, but occasionally it is necessary to clean off the surface of the mercury with a piece of filter paper wrapped around the end of a glass rod. The mercury in the instrument after two and one-half years is as bright and shiny as when first introduced.

The temperature of the mercury in the barometer cannot readily be determined by direct measurement. With fairly constant temperature as secured by control of the room temperature, the mercury temperature may be measured with sufficient accuracy by thermometers placed near the barometer. To simulate the conditions in the barometer, the bulbs are immersed in test tubes filled with mercury as can be seen in Figures 28, 29 and 30. One is placed well above the upper surface, one below the lower surface and two in the central regions. They are arranged to effectively surround the barometer as much as possible. The thermometers were compared with a thermometer which had been certified at the Bureau of Standards. They were found to read correctly to $\pm 0.05^{\circ}C$. It will be shown later that for an accuracy of ± 0.02 mm. in barometric height, the mercury temperature needs to be known only to $\pm 0.1^{\circ}$. It was found that a gradient of about 0.4° existed between the upper and lower thermometers. The readings of the two thermometers near the center agreed within a few hundredths of a degree with the average of the other two. The use of the average of all four readings then probably represents the average barometer temperature within $\pm 0.1^{\circ}$.

The distance between the upper and lower mercury levels is measured by means of the two-telescope cathetometer and the meter bar also visible in Figure 28. The telescopes are first sighted on the mercury meniscuses and by rotation of the cathetometer shaft and observations on the meter bar, the difference in elevation of the mercury levels is obtained. In order to improve the images of the meniscuses, two blackened brass sleeves were placed around the upper and lower limbs as indicated in Figures 29 and 30. By means of adjusting screws these can be moved until in each case the plane of the bottom of the sleeve is just above the mercury surface. In this manner, using diffuse illumination from behind, stray reflections are avoided and sharp meniscus images are realized. Usually about 0.1 mm. separates the plane of the end of the sleeve from the plane of the major portion of the mercury surface.

Before considering the proof of operation as a Normal Barometer and the application to the steam point resistance measurements, it is advisable to deal with the cathetometer and the meter bar as the quality and performance of these pieces are vital to the success of the barometric measurements.

The Cathetometer and Meter Bar.

Introduction. The cathetometer was designed and constructed with the advice and mechanical assistance of Mr. Walter Mintel, an expert instrument maker of the University.* It embodies features of instruments built by the Société Génevoise and the Gaertner Scientific Corporation, as well as a precision cathetometer recently described by Moon[57] of the Bureau of Standards.

A properly designed precision cathetometer should include provisions for aligning the shaft on which the telescopes are mounted in as truly a vertical position as possible. In addition, it should provide adjustments for orienting the geometrical axes of the telescopes at right angles to the vertical axis of rotation. Indicating equipment must also be included to show the extent of realization of these conditions. In addition to these requirements, a number of complicating factors must be considered. The vertical shaft may not be perfectly straight. Consequently when one portion of its length is brought into correct vertical adjustment, another portion may be inclined. Also the human factor must be considered in regard to the excellence of adjustment which will be governed by the skill and patience of the operator as well as by the mechanical perfection of the parts. The conclusion to be drawn from such considerations is that the indicating equipment will in all practical cases show that the shaft and telescopes are not in perfect alignment for all possible settings.

* The University is fortunate in having as one of its employees a man skilled in the design and construction of precision instruments of this character, a portion of his training having been obtained with the Gaertner Scientific Corporation.

The relation between the extent of these deviations and the error thereby introduced into measurements made with the cathetometer must be considered in precision work. Marek[55] investigated these questions in 1884 and reached some valuable conclusions. Considering that the axis of rotation and the geometrical axis of the telescope were slightly skew and neither one in proper alignment, he developed a relation to express the actual difference in elevation of two objects which might appear to be at the same elevation when viewed with this maladjusted instrument. The formulation utilizes the readings on the level placed on the telescope, the angular rotation of the shaft and the distances from the center of the objective to the axis of rotation and to the objects being viewed. The development is based on a fundamental relation of spherical trigonometry, but its examination is complicated because of a serious discrepancy in the early stages of the derivation and certain peculiarities in the style of printing used in the published article. It was found that an attack on the problem using relations of solid analytical geometry yielded a solution which could be transformed into the final result obtained by Marek. By working from his correct conclusions it was possible to trace back to the correct starting relations and to interpret the notation employed.

The application of this analysis to the design of a new instrument is limited by the fact that the values for some of the quantities in the Marek equation cannot be estimated until the instrument is completed and tests performed. However, certain generalizations are possible. The distances from the center of the objective to the axis of rotation and to the object should be as short as possible. The first is limited by the fact that the weight of the telescope should be evenly distributed with respect to the vertical shaft in order to avoid uneven strains in that member. In the instrument which Marek designed the distance was 136 mm. It usually ranges between 100 and 150 mm. in high quality instruments. The distance from the center of the objective to the object will depend on the objective lens and the tube length of the telescopes. These should be selected with due consideration to the nature of the objects to be viewed. If glass tubes or other items must intervene between the objective and the object, the working distance must be long enough to accommodate them. Marek selected a lens and tube length which had a working distance of 165 mm. The working distance selected for the apparatus to be described below is 54 mm.

Another point to be observed in making comparative length measurements is to place the objects being examined as close together as possible in order to minimize the angular rotation of the shaft. This is a desirable condition brought out by the Marek equation.

As regards the level readings which also enter into the Marek equation, it has been general practice in the construction of precision cathetometers to use levels with a high sensitivity, about 5" to 20" of arc per division of bubble movement. Errors of roughly 0.001 mm. might be introduced into relative elevation readings with a high quality instrument such as Marek used if variations of 2" of arc in level readings were experienced in rotation of the shaft. A level with a sensitivity of 10" of arc per division would clearly indicate such variations. The levels in the instrument to be described have approximately that sensitivity. As a matter of fact even more strict limitations were imposed upon the construction of the cathetometer for this work by the accuracy required in the measurements of the lengths of the conductivity cells than by the requirements involved in the measurement of the barometer. As will be shown later as well as in the next section, the instrument constructed by Mr. Mintel has thus far met all the requirements imposed upon it in both connections.

Description of the cathetometer. The instrument is shown in Figure 28 and a close up of the lower telescope is shown in Figure 32. These figures represent its final form as used except that the micrometers have been inverted in order to place the drum above the box and thereby properly distribute its weight on the bearings. The vertical shaft, 3.2 cm. in diameter and about 1.15 m. in length, was donated by the Ford Motor Company. The steel is identical in composition and heat treatment with the type used in the manufacture of the famous Johansson Gage Blocks. It is claimed to be as free from strain or liability to gradual change as can possibly be realized

at the present time. Due to the corrosive fumes of the chemical laboratory, it was given a light plating of cadmium. The lower end of the shaft is fashioned to a 60° taper and it seats in a matching hardened steel socket which is in turn suitably fastened to a cast iron bracket projecting from the concrete pillar which in turn projects from a solid concrete block visible in Figure 28. At the upper end of the shaft, a steel ball is fastened. This seats in a brass socket fastened to another cast iron bracket projecting from the concrete pillar. The upper and lower sockets can be adjusted in all possible directions by means of suitable screws in the cast iron brackets. In this way the shaft can be aligned so that it rotates on a vertical axis. Best operation is secured by permitting the upper socket to support the weight of the shaft and the telescopes and then to raise the lower socket until it just touches the tapered point of the shaft and removes all freedom of horizontal movement.

The telescopes as constructed have a fixed tube length of about 180 mm. Focusing is obtained by moving the telescopes back and forth in suitable slides, visible in Figure 32, by means of rack and pinion adjustments. When the slides are in the central position, the distance from the center of the objective to the axis of rotation of the shaft is 120 mm. The objective lenses were obtained from the Gaertner Scientific Corporation and as mounted they have a constant working distance of 54 mm. The original lens mountings were not satisfactory as the optical centers of the objectives did not lie in the geometrical axes of the telescopes. The slightest rotation of the telescopes about their axes would cause an apparent vertical shift in an object viewed. Mr. Mintel remounted the objectives so that the optical centers and geometrical axes appear to coincide perfectly. A magnification of 4.1 times is obtained in the plane of the cross hairs of the filar micrometers. These were also procured from the Gaertner Corporation. They were defective in that the geometrical centers of the micrometers did not coincide with the optical centers of the eyepieces. A reconstruction of the mountings brought the points in question into coincidence. The movable cross hairs which are separated by about 20 microns are operated by a screw of 0.25 mm. pitch. The drum at the end of the screw is divided into 100 divisions. A movement of one division of the drum measures a distance of 0.0006 mm. in a vertical sense in the plane of the object under examination.

The telescopes may be adjusted for leveling in a plane parallel to the axis of the shaft by means of suitable attachments (which, however, are not readily discernible in the various photographs). The level vials were obtained from the G. and L. E. Gurley Company. After mounting them in suitable holders to permit their use as striding levels, they were calibrated on a level tester. This consisted of a micrometer caliper reading directly to 0.1 mm. mounted so that it could raise or lower one end of a 74 cm. lever arm made of brass rod. The fulcrum of the lever was at a knife-edge. The levels were placed astride the bar and the movements of the bubbles compared with the measured angular displacements obtained by manipulating the micrometer caliper. The quality of the levels is excellent. No. 1 has an average sensitivity of 10.4" per division and No. 2 has a corresponding value of 9.4" per division. These values may be applied by any particular division with an accuracy of $\pm$0.3" which is ample in the light of the requirements of the Marek equation.

The telescopes and adjusting devices are mounted on sleeves of brass which fit nicely on the steel shaft and are keyed to it so that rotation as a unit is secured. These sleeves or slides permit movement of the telescopes in a vertical sense. They are held at any desired elevation by auxiliary slides which can be clamped firmly to the shaft. The main and auxiliary slides are joined by an adjusting screw. A variety of adjustments are provided to bring an object into the field of view of one of the telescopes. The release of a clamping screw at the base of the shaft permits free rotation. If this screw is tightened, fine adjustment of rotation is secured by a suitably mounted thumbscrew. The clamping slide on the shaft may be released and the telescope unit moved up or down to approximately the desired position. The clamping slide may then be fixed in position and the final movement secured with the thumbscrew which joins the two slides. With the object once in the field of view, it may be brought into focus by sliding the telescope back

and forth in the usual manner.

The method of illumination used in conjunction with the telescopes depends upon the character of the object. The mercury surfaces of the barometer are illuminated from behind, but in the axes of the telescopes. Some of the light passes between the blackened sleeves and the mercury and then into the telescopes. Consequently it serves to define the location of the mercury surfaces. In the case of the meter bar, a so called vertical illuminator as used by Moon is employed. This consists of a light source which emits a beam at right angles to the telescope axis. The light is bent through 90° in the telescope itself and directed through the objective at the object. It is then reflected back through the objective and some of it passes the reflector, which is transparent, and continues on to the ocular. This is one of the conventional means of meter bar illumination. The device may be seen in Figure 32 mounted on the telescope tube near the objective. A small six volt flashlight bulb operated at a lower voltage to diminish the light intensity, a condensing lens, and a Wratten light filter No. 59 giving a restful, yellow-green light are contained in the side tube. A 5/8 inch No. 1 cover glass to serve as the reflector is mounted in the telescope tube and is provided with adjustments for setting it at the proper angle to give the best illumination as found by trial. Cover glasses which were free of superficial flaws were examined with a small optical bench. Those which were found to be free of striae were selected for use in the illuminators.

Before discussing the performance tests on the cathetometer, a description of the meter bar and its support is necessary since the meter bar is used for many of the tests on the cathetometer.

The meter bar and its support. The meter bar of the conventional H type is made of brass with inlaid silver scale. It was manufactured by the Gaertner Scientific Corporation and bears their number 56. The silver strip in the neutral axis of the bar is graduated in millimeters from zero to one thousand and at each end an additional millimeter is graduated in 0.1 mm. intervals. The quality of the lines is good, but is not of the best. The lines are 15 to 25 microns in width and were not cut with a properly sharpened tool. As a consequence the edges of the lines are slightly roughened and the bottoms of the grooves are flat. This results in a strip of light running through the center of the slightly ragged dark image of each line. A properly engraved line is free of these defects which increase the difficulty of obtaining proper focus. The bar was sent to the Bureau of Standards for certification to the highest accuracy compatible with the quality of the piece. The total length, the ten decimeter intervals, the first ten centimeter intervals, the first ten millimeter intervals and the one-tenth millimeter intervals at the end marked zero were measured. All of the values are given as correct to 0.003 mm. This is sufficiently accurate for any use to which the bar may be put in the complete determination of the standard conductivity values.

In use, the meter bar is supported on a stand shown in Figure 33. A square tube fits around the bar and may be clamped in place at any point along the length of the bar. Two steel knife-edges fastened to this tube rest in V blocks on the stand. Set screws at the lower end hold the bar in position.

For adjusting the bar in a vertical position, a plumb line may be used with sufficient accuracy. If the bar were inclined and the length of an object found by observation on the object and on the meter bar using the cathetometer, the actual length would be less than the measured length. This difference can be expressed as $(1 - \cos \alpha)L$ where α is the angle of inclination of the bar to the vertical and L is the measured length. The most accurate measurements to be made with the cathetometer are the lengths of the glass tubes to be used as conductivity cells. In keeping with the limits of error set for this work, these lengths should be measured accurately to 0.001% of their values. In that case $(1 - \cos \alpha)$ should not exceed 0.00001 and consequently α should not be greater than 18' nor need it be less than 10'. A value of α of 15' corresponds to a departure from the vertical of 4 mm. in one meter, an easily detected distance. Experience demonstrated that it is readily possible to adjust the bar for verticality within 5'.

In very precise work, if the meter bar is mounted in a vertical position, it is necessary to consider the elongating effect of the weight of the

bar itself. The calibration at the Bureau of Standards is carried out with the bar mounted in a horizontal position at the so called neutral points, the 23 and 77 cm. lines. Consequently a correction must be considered if the bar is supported in some other position.

The bar in this set up is normally hung with the zero mark at the bottom and with the top of the clamping tube at the 70 cm. mark and the bottom at the 65.8 cm. Under such conditions, the part of the bar from 0 to about 67.9 cm. tends to elongate and from 67.9 to 100 cm. it tends to shorten. For any point on the bar the deformation may be considered as the sum of two factors. Figure 34 represents the bar mounted at A - A. Consider a point at a distance x below A - A as at B - B. The effect of the portion of the bar below B - B may be treated as a weight concentrated at B - B. The length of this portion is (L - x) where L denotes the distance from the support to the end of the bar. Then if w is the weight per unit length, the weight concentrated at B - B is equal to w(L - x). The stress, S, may be expressed then by the equation

$$S = \frac{w(L - x)}{A}$$

where A is the cross sectional area of the bar. The strain, δ, or unit extention of the bar is defined as

$$\delta = \frac{S}{E}$$

where E is Young's Modulus for the material of the bar. Consequently in this instance δ may be expressed as

$$\delta = \frac{w(L - x)}{AE}.$$

The extension for the length x or Δ_1, may be expressed as

$$\Delta_1 = \delta x = \frac{wx(L - x)}{AE}.$$

This phase of the problem corresponds to the case of a weightless wire of length x, cross sectional area A and Young's Modulus E at the end of which is hung a weight w(L - x).

The second factor in the total distortion is due to the portion of the bar above B - B and below A - A. Consider the division of this section into a number of elements of infinitesimal thickness dx'. For an element at a distance x' below A - A as in Figure 34, the strain, as in the consideration of the first factor, is $\frac{w\,dx'}{AE}$ and the extension at B - B due to this small weight is expressed as

$$d\Delta_2 = \frac{wx'dx'}{AE}.$$

The total deflection at B - B due to all these strips may be obtained by a summation or integration from x' = 0 to x' = x of the expression $\Delta_2 = \int_0^x \frac{wx'dx'}{AE}$

Thus $$\Delta_2 = \frac{wx^2}{2AE}.$$

The total extension at B - B is equal to $\Delta_1 + \Delta_2$ or $\frac{wx(L - x)}{AE} + \frac{wx^2}{2AE}$, which may be combined as $\frac{wx}{AE}(L - \frac{x}{2})$.

If the total weight, W, of the length L is known, a transformation may be made, substituting W/L for w. Thus,

$$\Delta = \frac{Wx}{AEL}(L - \frac{x}{2}) = \frac{Wx}{AE}(1 - \frac{x}{2L}).$$

The section above A - A may be treated in similar fashion and the result obtained is identical in form although the deformation is one of compression instead of elongation.

From the dimensions of the bar, A was found to be 3.85 sq. cm. For the part below, A - A, W is approximately 2220 grams and L is 68.7 cm. For the part above A - A, W is approximately 1065 grams and L is 32.9 cm. Young's Modulus for brass is $9.2 \cdot 10^{11}$ dynes per cm.^{2} Then Δ at reading 0 cm. is $2.13 \cdot 10^{-4}$ mm. and at reading 100 cm. it is equal to $0.48 \cdot 10^{-4}$ mm. The deformations decrease as reading 67.9 is approached being 0 at that point.

It is evident from these results that the deformation of the bar due to its own weight is of no consequence in length measurements made with an accuracy of 0.003 mm. Such an accuracy is sufficient for the barometric readings and the determination of the lengths of the glass cells.

In the use of a brass meter bar, it is necessary to consider the relation between length and temperature. The meter bar has a coefficient of expansion of 0.0000193 per degree Centigrade as determined by the Bureau of Standards. None of the glass tubes to be accurately measured are longer than 40 cm. If this length is measured to $\pm$0.001% or $\pm$0.004 mm., the allowable temperature variation is $\pm 0.5^\circ$ from the temperature at which the corrections apply. Since the room can readily be controlled to $\pm 0.3^\circ$, no appreciable error is introduced from this source. To insure the accuracy, however, the temperature of the

bar should be determined by means of two or three mercurial thermometers placed in close proximity.

Calibration of the filar micrometers. The readings of the filar micrometers are in terms of revolutions and fractions of revolutions of the micrometer screws. To be of utility, it is necessary to determine the tares of these instruments, that is the number of revolutions required to move the cross hairs from apparent coincidence with the image of one line on the meter bar to the image of some other line a known distance from the first. If the micrometer screws and bearings are mechanically perfect, this represents the complete evaluation of the micrometer characteristics. Unfortunately, micrometer screws, like all other types of lead screws, are subject to both periodic and progressive errors. The existence of such errors has been recognized for more than fifty years and a number of methods developed for their evaluation. It has been found impossible to completely eliminate these errors. The simplest method to determine them from the standpoint of both actual measurements and treatment of data was described by Gray[15] of the Bureau of Standards in 1914. Briefly, the method consists in measuring the actual movements of the cross hairs of one micrometer, the ocular removed, by means of the other telescope under which conditions the errors in the second screw are of no importance if they are reasonably small. Various length intervals are examined, five whole turns of the drum of the first micrometer, single turns and fractions of turns. If the errors prove to be regular in character, it is unnecessary to measure all the single turns and fractions. The results are expressed in terms of drum revolutions of the second micrometer. By exchanging micrometers the same process may be carried through for the second instrument. For convenience in determining the number of drum revolutions, the conventional strips with comb teeth are mounted in the micrometers. One revolution of the drum moves the hairs from one comb tooth to the next so that by counting the number of teeth passed, the whole number of revolutions may be quickly determined. The central tooth is numbered 30 for convenience and the remainder from 0 to 60. The convention selected in this work is that as the cross hairs appear to rise (actually they are moving downward), the drum readings increase. As constructed, approximately sixteen turns correspond to a 1 mm. interval on the meter bar. The micrometer screws were calibrated then from readings of twenty to forty revolutions. This covers about two-thirds of the field of each ocular.

The level holders to rest on the telescopes were originally constructed so that they could be reversed end for end. The average of the two bubble readings would then represent the departure of the geometrical axis of the telescope from horizontality. In the course of the micrometer calibration, considerable difficulty was experienced in obtaining reproducible level readings. To remedy this difficulty, the levels were rigidly fastened to the telescopes. A slight departure from a truly horizontal position would have an inappreciable effect on comparison measurements provided the departure remained essentially constant. The level holders were therefore clamped to the telescope tubes after first adjusting the telescopes to be horizontal to within 2". The clamps were adjusted to bring the level bubble reading to the center of the vial in each case. With such an arrangement there is no conveniently obtainable positive assurance that the telescope is horizontal even though the level reading may indicate that fact. By the method of mounting, the deviation from the horizontal position is probably not more than 5".

The proof that this method of mounting is satisfactory for measurements with an accuracy of $\pm$0.003 mm. will be found in the discussion of the performance tests on the cathetometer. If the level did not remain fixed with respect to the telescope, the tare value would change each time the telescope was adjusted to be supposedly horizontal and apparent variations in length intervals would be observed. It will be shown that the differences observed are inappreciable for this work for series of observations extending over several days.

It is possible to obtain reproducible level readings using the end-to-end reversal method, but the care and patience which must be exercised is very great. Only in exceptional cases where accurate adjustment to true horizontality is necessary would it be desirable to remove the clamps and use the levels in the reversal method.

The corrections for the screw errors are expressed in drum revolutions. The results obtained for the micrometer of the upper telescope indicated that the corrections in no case are greater than 0.01 revolutions and may be neglected. This corresponds to 0.0006 mm. on an object being examined and is therefore negligible in comparison with 0.003 mm., the highest required accuracy. In the case of the micrometer for the lower telescope the corrections in some portions are as large as 0.002 mm. on an object being observed and so must be considered. The corrections are given in Table 19 and were obtained from the suitably constructed graphs prepared according to the directions of Gray.[15]

The tares of the micrometers were obtained by measurements on the interval 0.0 to -1.0 mm. of the meter bar which had a value of 0.997 mm. according to the Bureau of Standards certification. Three measurements of this length with the lower instrument gave as corrected values 16.548, 16.572 and 16.556 revolutions. The average is 16.559 revolutions with a probable error of the mean of $\pm$0.005 revolutions. The tare value is obtained as 0.997/16.559 or 0.06021 mm. per turn with a probable accuracy of $\pm$0.30% or $\pm$0.00018 mm. The same interval was measured with the upper telescope and three values of 16.522, 16.454 and 16.509 revolutions were obtained. The average is 16.495 revolutions with a probable error of the mean of $\pm$0.013 revolutions. The tare value may be expressed as 0.997/16.495 or 0.06044 mm. per turn with a probable accuracy of $\pm$0.31% or $\pm$0.00019 mm. These values are sufficiently accurate for any length measurements of this work made with the cathetometer.

Performance tests on the cathetometer. The movement of the shaft in its bearings is excellent when in proper adjustment. Unfortunately the concrete pillar upon which the cathetometer is mounted has shown a gradual contraction which requires that the shaft be adjusted before making any careful measurements. It usually remains in adjustment for at least a day and then requires only minor changes to establish proper alignment. It was found possible to adjust the shaft so that no variations of more than 2" in the level readings were observed on rotation of the shaft. Also, the shaft is sufficiently straight so that no greater variations than 2" in level readings were observed on sliding the telescopes up and down. Therefore, in the light of Marek's work discussed earlier, the effect of skewness and lack of alignment of the telescope and shaft will not cause the observations on objects at the same level to be in error by more than $\pm$0.001 mm. To test this conclusion a series of observations on one line of the meter bar was made with the telescope intentionally inclined at various angles. The results indicated an apparent vertical shift of the line of 0.0074 mm. per division of bubble movement or 0.0015 mm. for 2" bubble movement as compared with 0.001 mm. as predicted.

Since the actual limit of accuracy of this complete assembly cannot be greater than $\pm$0.003 mm. due to the inaccuracies of meter bar certification, the observed bubble movements of 2" are entirely permissible.

It was found that the light bulb in the illuminators on the telescopes gave off sufficient heat to affect the level readings. In ten minutes after turning on the light, the end of the level holder nearest the illuminator had expanded sufficiently to cause a shift of 0.1 division. In fifteen minutes this had increased to 0.3 division. After several hours it had increased still more to 0.6 division. For precise work therefore the light should not be left on for more than ten minutes at a time.

To check the accuracy of the instrument for the determination of differences in level with a single telescope, a number of settings on lines were made, the shaft rotated through a variety of angles from 5° to 90° and on returning to the original position, no change greater than 0.001 mm. in movement of the shaft up or down could be discerned by reference to the cross hairs and the line being observed. This perfection of movement is important when comparative observations using only one telescope are being made. In observations such as on the meter bar and barometer, an actual shift in the elevation of the shaft is of no consequence as the only quantity of concern is the vertical distance between the two telescopes. That distance is unaffected by any vertical movements of the shaft in the bearings as long as the adjustments are made to remove all side play.

The precision with which the micrometer hairs can be set on a given line of the meter bar is indicated by a series of readings on the lines from 0.0 to -1.0 mm. using the upper telescope. The micrometer drum is always turned in the same direction in making settings in order to avoid the effects of backlash in the micrometer screws. The readings on the lines in this case were made in the order -1.0, -0.9, ... 0.0, 0.0, -0.1, ... -1.0, -1.0, -0.9 .... 0.0 mm. Three readings were thus obtained for each line. The maximum deviation for any individual reading was only 4.1 drum divisions or 2.5 microns and the average deviation calculated from all the deviations was 1.7 drum divisions or 1.0 micron.

The same data serve to indicate the precision with which a given length interval may be measured. Three measurements of each of the 0.1 mm. intervals from 0.0 to -1.0 mm. were obtained. The maximum deviation for any one of these measurements was 3.1 microns and the average deviation computed as the average of all the deviations was 0.9 micron. These values are of the same order of magnitude as those expressed above for the precision of setting on given lines. Together they indicate that the quality of the cathetometer is superior to the meter bar in that more precise measurements may be made with the former than are warranted by the known accuracy of the various length intervals of the bar.

The accuracy with which various intervals can be measured is indicated by the results presented in Table 20. The intervals noted in the first column were measured with both telescopes. The Bureau of Standard values are given in the second column and the results with the two telescopes in the remainder. These results were calculated from the observed numbers of revolutions of the micrometer screws using the tare values previously obtained, namely 0.06044 mm. per turn for the upper and 0.06021 mm. per turn for the lower micrometer. An inspection of these data indicates that the measured values agreed with the certified values in every instance within the limits of accuracy of certification, $\pm$0.003 mm.

The constancy of the tare values is shown by a second determination one month after the above values were obtained. Values of 0.06069 mm. per turn for the upper and 0.06020 mm. per turn for the lower were obtained. The difference for the upper corresponds to only 0.004 mm. in 1.0 mm. and for the lower, it is negligible. It is evident that for measurements to $\pm$0.003 mm., the tare values should be frequently redetermined.

From these various tests it may be concluded that the combination of the two-telescope cathetometer and meter bar may be used for measurements of length from 0.000 to 1000.000 mm. with an accuracy of $\pm$0.003 mm. determined on the basis of the instruments themselves provided the objects to be measured are ideally suited for observation.

The Measurement of Barometric Pressure. Since the cathetometer and meter bar assembly are satisfactory for use in accurately measuring differences in elevations, their application to the barometer, the accumulation of the data and the auxiliary measurements may be considered. For the immediate purpose of making conductivity measurements at 25°C., a barometer as accurate as the one described herein is not necessary. The instrument will be required, however, in future work at higher temperatures. For this reason, the factors which must be considered under those conditions will be dealt with here.

The barometer and meter bar were set as close together as possible to keep the angular rotation of the shaft at a minimum. Both were adjusted to verticality using a plumb line. In the case of the barometer this is unnecessary in so far as the mercury is concerned for it adjusts itself even though the barometer is inclined. However, with the barometer vertical, the possibility of error due to refraction of light by the glass tubing and consequent error in determining the apparent elevations of the mercury surfaces is minimized, and also, the focusing movements of the telescopes are reduced. The stands are placed so that in rotating from the barometer to the meter bar, very little focusing adjustment is needed. It was found that satisfactory observations on the mercury surfaces were obtained only when the telescope illuminator bulbs were turned off.

The procedure in making an observation is to raise the plunger and then carefully lower it to produce a rising meniscus in both limbs. The blackened sleeves are

then set to the best positions and the telescopes focused on the mercury surfaces. These manipulations usually cause appreciable oscillation of the mercury so a few minutes are allowed to elapse without disturbing the assembly. The four thermometers are read and the micrometer hairs set for coincidence with the images of the mercury surfaces. Due to the residual oscillation of the mercury this setting is uncertain by about ± 0.005 mm. The micrometer readings are recorded and then the shaft is rotated to permit sighting on the meter bar. The telescope illuminators are turned on and the micrometers adjusted to obtain readings on the nearest lines. Tests indicated that the heat of the body caused an increase of about 0.03° in the readings of the thermometers of the barometer set up during these measurements. This is a sufficiently small change so that in practice the thermometer readings are made but once, just before sighting on the mercury.

The observed revolutions of the micrometer drums are converted to millimeters using the tare values and then added to or subtracted from the nominal values of the lines on the meter bar. For the barometric measurements interpolation between the decimeter interval correction values gives with sufficient accuracy the correction to be applied to the meter bar readings. Whether or not the difference between the two corrected readings represents the actual barometric height, is a point that requires further consideration.

One of the factors which may contribute to this uncertainty is the possibility of gas remaining in the upper evacuated space. The method of measurement of the effect of this gas is generally attributed to Arago. It consists in measuring the barometric height and then raising the mercury to diminish the volume of the residual gas space and making another barometric reading. If any gas is present in the vacuum space, upon compression it will exert a greater pressure and the observed barometric height will be less than it was in the first case. From a knowledge of the gas volumes in the two cases, the temperature and the differences in readings, the correction may be calculated for any position of the upper mercury meniscus at any temperature. It is generally desirable to have available another barometer of equal accuracy upon which simultaneous readings, but with constant upper meniscus level, may be made. This would serve to eliminate the possibility of an indication of residual gas pressure resulting from an actual change in barometric pressure. Since no barometer of equal accuracy was available, it was necessary to carry out the tests for the presence of residual gas when the weather was clear and the pressure was very steady.

The volume of the evacuated space was found by measurement made before the barometer was assembled. Two etch marks, m and n, were made around the upper limb in Figure 31 and a third, p, around the capillary tube. The portion of the barometer between points x and y was mounted in an inverted position and the weights of mercury needed to fill the bulb between the etch marks were found. A consideration of the Arago method indicates the accuracy needed in determination of the residual gas volume. Assuming that this volume were changed from 100 $cm.^3$ to 50 $cm.^3$ and a change in barometric reading of 0.02 mm. was observed, the residual gas volumes would need to be known to ± 1 $cm.^3$ in order to evaluate the residual gas pressure to ± 0.001 mm. The volumes between m and n and between n and p were determined as 35.0 ± 0.0 $cm.^3$ and 27.3 ± 0.0 $cm.^3$ respectively. The determination of the volume between m and n serves to calibrate the bore of the tubing assuming that it is uniform.

The completed barometer was tested for residual gas using a variety of plunger positions. Successive readings were obtained as rapidly as possible without sacrifice of care in the manipulations. The plunger was inserted at various depths in order to vary the residual gas space at least twofold. On no occasion was there residual gas which would require a pressure correction of 0.02 mm.

The effect of mercury vapor is of no consequence as at 25° the vapor pressure of mercury is only about 0.002 mm.

Another factor which can influence the accuracy of measurement of the barometric height is refraction of the light from the mercury surface by the glass wall of the barometer. If appreciable refraction occurred due to inclination of the barometer, the mercury surfaces would not appear to be at their actual elevations. A test of this effect was made by mounting a wire about 0.08 mm. in diameter in a horizontal position behind the lower tube and sighting upon it in three positions: at either side of the glass tube and through the glass. If refraction occurred, the central observation would not agree with the mean of

the other two. The results agree within five microns so that no correction is needed. The upper tube cannot be conveniently tested, but since it is from the same lot of glass tubing and the plumb line indicates essential parallelism between the upper and lower limbs, it may be assumed that the error is negligible for the upper limb as well.

The capillary depression of the mercury surfaces which can affect the difference between the observed and true barometric heights has been made negligibly small by the use of 40 mm. glass tubing for the upper and lower limbs.

It is evident from these considerations that this apparatus can be used to measure barometric heights with an accuracy of ± 0.02 mm.

In order to calculate the steam point temperatures, the pressures must be converted to the conditions represented in the definition of standard atmospheric pressure. The pressure must be expressed in terms of mercury having a density of 13.5951 grams/cm.^{3} and subject to a gravitational acceleration of 980.665 cm./sec.^{2} The conversion to these conditions may be made by multiplying the observed barometric height by two ratios. The first is the ratio of the gravitational acceleration constant at the location of the barometer to 980.665 cm./sec.^{2}, the value used in the definition above. The second ratio is that of the density of the mercury at the temperature of measurement to 13.5951 grams /cm.^{3}, the value given in the definition. Specific gravities referred to air free water of maximum density may also be used.

The calculation of the gravitational constant at any locality may be made using the equations given in the International Critical Tables.[25]

$$g_0 = g_{45}(1 - 0.002637 \cos 2\varphi + 0.000006 \cos^2 2\varphi)$$

and

$$g_H = g_0 - 0.0003086\ H,$$

where g_{45} is equal to 980.621 cm./sec.^{2}, g_0 is the gravitational constant at sea level in latitude φ and g_H is the value at elevation H and latitude φ. The Ann Arbor Astronomical Observatory is located at latitude 42°16'48.7" N. The Chemical Laboratory may therefore with sufficient accuracy be stated to lie at latitude 42°16'30" N. The Buildings and Grounds Department supplied the elevation of the floor of the southwest entry into the Chemical Laboratory as 882.10 ft. above sea level. After conversion of this to meters and correction for the location of the barometer with respect to the floor of the entry, the value of H is obtained as 269.3 meters. The value of g_H or the gravitational constant at the foot of the barometer is 980.298 cm./sec.^{2} The first correction ratio has a value, therefore, of 980.298/980.665 or 0.999626.

Marek[54] has shown that the density of carefully purified mercury agrees within $\pm 0.001\%$ with the generally accepted values for the purest material. Consequently it was deemed unnecessary to determine the density of the mercury used since it was carefully purified and an error of $\pm 0.004\%$ in its value would influence the observed barometric pressure by only ± 0.02 mm.

The value of 13.5951 grams/cm.^{3} for the density of pure mercury represents the value at a temperature of 0°C. and a pressure of one standard atmosphere. If the pressure were reduced essentially to zero atmospheres as at the upper end of the barometer, the density would be lowered. The coefficient of compressibility of mercury is approximately $3.8 \cdot 10^{-6}$ per atmosphere. Consequently the density of the mercury would decrease by about 0.00038% from the bottom to the top of the barometer. The difference between the pressure recorded by an actual mercury barometer at 0°C. and a hypothetical barometer in which the density of the mercury is invariant, is one-half of this density difference or 0.00019%. Therefore, although the standard atmosphere is defined in terms of this hypothetical barometer, it can actually be measured with a Normal Barometer by application of the correction for the variation in density. The desired limit of error in the pressure measurement for this work, namely ± 0.02 mm., amounts to only 0.0027% of the average observed pressure. Consequently the density of the mercury may be assumed to be uniform from the top to the bottom of the barometer without introducing an appreciable error into the measurements.

The density values used are those given in the International Critical Tables[26] as the most probable values referred to air free water of maximum density. They more properly should be designated as specific gravity values. At 20° the values given is 13.5463 grams/cm.^{3}, at 25° it is 13.5340 grams/cm.^{3} and at 30° it is 13.5218 grams/cm.^{3} The value of 13.5951 grams/cm.^{3} used in the definition of the standard atmosphere is the density at 0°. The specific gravity referred to air free water of maximum density may be obtained by dividing by

0.999973 grams/cm.^{3}, the maximum density of water. The result is 13.5955. The second ratios are therefore 13.5463/13.5955 at 20°, 13.5340/13.5955 at 25° and 13.5218/13.5955 at 30°.

It is convenient to multiply the two ratios together and obtain a single factor by which the observed barometric height must be multiplied. At 20° the factor is 0.99601, at 25° it is 0.99510 and at 30° it is 0.99421. Linear interpolation may be used with sufficient accuracy near 25°. An analysis of these factors indicates that the barometer temperature must be known to ±0.1°C. in order to determine the pressure with an accuracy of ±0.02 mm.

A sample calculation may be offered to illustrate how the various observations and corrections discussed are utilized in determinations of the barometric pressure with the apparatus described.

Data: Temperatures, reading from top to bottom, 25.42°, 25.20°, 25.12° and 24.93°.

Micrometer readings:

On upper mercury surface	31.829
On 859 mm. line	31.289 and 31.251, mean 31.270
On lower mercury surface	30.464
On 117 mm. line	30.494 and 30.470, mean 30.482

Calculations:

Upper mercury surface.
(31.829 - 31.270) = 0.559
(0.559) (0.06044) = 0.034 mm.
The line is above the mercury, therefore 859 - 0.034 or 858.966 mm. is the nominal reading.
Interpolated correction value = +0.040 mm.
Corrected reading = 859.006 mm.
Lower mercury surface.
(30.482 - 30.464) = 0.018
(0.018) (0.06021) = 0.001 mm.
The line is below the mercury, therefore 117 + 0.001 or 117.001 mm. is the nominal reading.
Interpolated correction value = +0.006 mm.
Corrected reading = 117.007 mm.
Observed barometric height = 859.006 - 117.007 = 741.999 mm. at a mean temperature of 25.17°
The correction factor to convert to standard conditions is 0.99508. The corrected reading is, therefore, 738.35 ± 0.02 mm.

Results of the steam point determinations.

Three successful series of steam point measurements were made, all under as nearly ideal conditions as possible. Alternate readings of pressure and thermometer resistance were made. The heating current for the hypsometer and the residual gas volume in the barometer were varied to demonstrate that these factors had no appreciable bearing on the results. The data for the pressure-time curves are presented in Table 21 and plotted in Figure 35. The time of pressure readings was taken just before sighting on the mercury surfaces and the time of resistance readings was taken as the average of the times at the start and conclusion of the resistance measurements. The pressures corresponding to the time of resistance readings were determined from the time-pressure curves and have been tabulated in the fourth column of Table 21. The temperature corresponding to each pressure was computed by means of the equation presented by the General Conference of Weights and Measures in 1927. The calculated temperatures are presented in the fifth column of Table 21.

The comparison of these measurements is best made by use of the relation of thermometer resistance and temperature. The resistances at the ice and sodium sulfate points when combined with the values for each of these steam points permit a calculation of the thermometer constants.

The constants in the equation

$$R_t = R_0(1 + At + Bt^2)$$

may be calculated by substituting the measured values of the ice, sodium sulfate and steam point resistances and the corresponding temperatures and solving the pair of simultaneous equations for A and B. The process is a laborious one and the equation obtained is awkward to use in the determination of other temperatures. In 1887 Callendar[6] proposed the now widely used Callendar equation

$$t - pt = \delta\left[\left(\frac{t}{100}\right)^2 - \left(\frac{t}{100}\right)\right].$$

This equation may be derived from the fundamental equation given above. In this derivation the terms employed are: pt, called the platinum temperature, is equal to $\frac{(R_t - R_0)100}{R_{100} - R_0}$ and is a linear function of the resistance; δ, which is a constant for a given thermometer and usually has a value of about 1.5, is defined as $\frac{-10000\ B}{A + 100\ B}$; c, called the fundamental coefficient

has the value $\frac{R_{100} - R_0}{100\ R_0}$.

If t is equal to 100, the equation

$$R_t = R_0(1 + At + Bt^2)$$

takes the form

$$R_{100} = R_0(1 + 100\ A + 100^2 B)$$

which may be transformed into

$$\frac{R_{100} - R_0}{100\ R_0} = A + 100\ B.$$

By definition this is also equal to c, the fundamental coefficient.

Also, $$pt = \frac{100\ R_0(At + Bt^2)}{R_{100} - R_0}$$

or $$pt = \frac{At + Bt^2}{c}$$

since $R_t - R_0 = R_0(At + Bt^2)$ and $\frac{100\ R_0}{R_{100} - R_0} = \frac{1}{c}$.

By definition $\delta = \frac{-10000\ B}{A + 100\ B}$

or $$B = \frac{-\delta c}{10000}$$

and therefore $$A = c + \frac{\delta c}{100}.$$

The equation $pt = \frac{At + Bt^2}{c}$ becomes

$$pt = (c + \frac{\delta c}{100})\frac{t}{c} - \frac{\delta c t^2}{10000\ c}$$

or $$pt = t + \frac{\delta}{100}t - \frac{\delta}{10000}t^2$$ which may be transformed to $t - pt = \delta\left[(\frac{t}{100})^2 - (\frac{t}{100})\right]$ as originally proposed by Callendar.*

The comparison between the steam point measurements was readily made by using the Callendar equation and calculating the values of δ and R_{100} from the data of Table 21 for each value of temperature and resistance in conjunction with the results of the ice point and sodium sulfate point measurements. The values for δ and R_{100} have been tabulated in the sixth and seventh columns of Table 21. The average value of R_{100} is 35.48519 units with a probable error of the mean of $\pm$0.00004 units corresponding to $\pm 0.0004^\circ$. Since the maximum deviation is only 0.00032 units or 0.0032° it is evident that this is a considerable improvement over the fortuitous errors of 0.005° reported by Mueller and Sligh.[60]

A set of values for R_0, $R_{100} - R_0$ and δ for a calorimetric resistance thermometer used at the Bureau of Standards were recently published by Jessup and Green.[30] The changes observed in R_0 were gradual amounting to only 0.0024 ohm in thirteen years. In terms of temperature this change represents only 0.024°. From August 1931 to September 1932, the value of R_0 changed by 0.0002 ohm or an equivalent of 0.002°. On the basis of this evidence it is justifiable to assume that the values of resistance at the ice and sodium sulfate points as determined in this work correspond within a few ten thousandths of a unit

* A number of discrepancies exist in the literature relative to this derivation. The actual value of A is positive and varies from 0.002 to 0.004 and is very much larger in magnitude than 100 B which is negative and of the order of -10^{-5}. The value of δ as defined above then becomes a positive quantity. In the original article Callendar[6] defined δ as $\frac{10000\ B}{A + 100\ B}$ instead of as $\frac{-10000\ B}{A + 100\ B}$ yet he expressed a characteristic value of δ as 1.5.

Sligh[77] in 1921 also defined δ by the expression $B = \frac{c\delta}{100^2}$ whereas the actual relation is $B = -\frac{c\delta}{100^2}$, yet he referred to δ throughout the article as a positive quantity.

In 1932 G. S. Callendar[5] in dealing with this subject, quoted for D which is merely $10^{-4}\delta$ the value $\frac{B}{A + 100\ B}$. In the next sentence he states, "As pt is less than t, when t is greater than 100, B has a negative value...." In a footnote on the same page he refers to a typical value of D as 0.00015 which is patently inconsistent.

None of these errors in sign are at all serious because in each case mentioned the correct Callendar equation has finally been used. Such errors are disconcerting, however, when making careful examinations of the articles.

to the actual values at the time of the steam point measurements made about a year later. Such resistance changes would have a negligible effect on the differences between the various R_{100} values although they would introduce the same error into all of them. Consequently the constants in the thermometer equations as calculated are not as reliable as they would be if all three calibrations were carried out within a few months.

From the average values for R_{100} together with the average experimental values at the ice and sodium sulfate points, the constants of the Callendar equation were calculated. The equation may be expressed as

$$t - \frac{R_t - 25.50569}{0.0997950} = 1.472\left[\left(\frac{t}{100}\right)^2 - \left(\frac{t}{100}\right)\right]$$

for this thermometer. The constants of the fundamental equation were also calculated and it takes the form

$$R_t = R_0(1 + 0.00397033\ t - 0.000000576\ t^2).$$

Conclusion.

The results of these measurements indicate that the thermometer resistance at the steam point may be determined with the apparatus assembled for the purpose with an accuracy of about $\pm 0.0005^\circ$ provided that several series of measurements are made.

It may also be concluded that the thermometer satisfies the requirements laid down by the General Conference in 1927. According to their specifications, the ratio R_t/R_0 shall not be less than 1.390 for t equal to 100°. In this case it is 1.391. Similarly for t equal to 444.6°, the sulfur point, the ratio shall not be less than 2.645. The calculated value is 2.651 obtained by using the constants of the thermometer as given above to determine what the sulfur point resistance would be.

The accuracy of temperature measurements at 25°.

It is important to consider the influence of the uncertainty of the fixed point measurements upon temperature determinations at 25°. This may be most readily accomplished by finding the equation for a measured temperature, t, expressed in terms of the various resistances and temperatures with the constants A and B of the general equation eliminated. If R_N is used to denote the resistance at t_N, the sodium sulfate point and R_S represents the resistance at t_S, the steam point, then two equations may be written,

$$R_N = R_0(1 + At_N + Bt_N^2)$$

and

$$R_S = R_0(1 + At_S + Bt_S^2).$$

The values of A and B may be found by solution of these simultaneous equations and upon substitution in the general equation $R_t = R_0(1 + At + Bt^2)$, the equation

$$R_t = R_0 + (R_N - R_0)\frac{t}{t_N} + \frac{(R_S - R_0)(t^2 - t_N t)}{(t_S^2 - t_S t_N)} + \frac{(R_N - R_0)(t^2 - t_N t)}{(t_N^2 - t_S t_N)}$$

is obtained. The effect of the uncertainties in all the measured quantities upon the value of t may be found by partial differentiation of t with respect to each in turn. These partial differential equations may be evaluated by assigning finite values to the various partial derivatives and calculating the uncertainties in t. The values used in these calculations and the resultant accidental errors are to be found in Table 22. The value of ΔR_0 was chosen as ± 0.00004 units rather than ± 0.00003 units in order to include the uncertainty in reproducing the ice point which would otherwise be neglected in the calculations. It is evident that the greatest error is produced by the uncertainty in reproducing the sodium sulfate transition temperature.

The effect of all of the errors on the value of t may be found by solving the equation

$$\Delta t = \pm\sqrt{(\Delta t)^2_{R_t} + (\Delta t)^2_{R_0} + (\Delta t)^2_{R_N} + (\Delta t)^2_{R_S} + (\Delta t)^2_{t_N} + (\Delta t)^2_{t_S}}$$

The calculated result is $\pm 0.0006^\circ$. In other words, with the equipment available it is possible to measure the actual temperature of the oil thermostat with an accuracy of $\pm 0.0006^\circ$ on the International Temperature Scale. This corresponds to an uncertainty in the standard conductivity values of $\pm 0.0012\%$.

Since the uncertainty in the control of the thermostat temperature introduces an error of about $\pm 0.001\%$ in the conductivity values, the combined uncertainty due to the maintenance and the measurement of the temperature at 25° amounts to $\pm 0.0016\%$ in terms of the final conductivity values.

In addition, as pointed out earlier, there exists an uncertain systematic error in the sodium sulfate transition temperature for which correction can be made if and when more accurate information becomes available. From the work of Buckingham and of Dickinson and Mueller and the unpublished results of Shedlovsky, it is believed that this error will not exceed 0.003 to 0.004°. The resulting correction to the temperature in the neighborhood of 25° will be not more than 0.0025 to 0.003° and that in the conductivity will not exceed 0.005 to 0.006%.

EQUIPMENT FOR THE PREPARATION OF SOLUTIONS

The Balances, Weights and Weighings.

Recognized practice in precise conductivity measurements at the present time includes the preparation of the solutions by weight methods rather than by volume. The accuracy required in the weighings to keep the error in the final conductivity values from this source at 0.001% may be determined from the relation between conductivity and concentration. In the case of KCl solutions, the proportionality is approximately a direct one so that the solutions must be prepared with an accuracy of ± 0.001% in concentration. It has been indicated in previous sections that 1.0, 0.1 and 0.01 D KCl solutions are used at the present time as conductivity standards. Of these, the 0.1 D solution possesses the greatest applicability and for that reason was selected for the first measurements in the present work. It is to be borne in mind that the resistance and temperature measuring equipment and the thermostat previously described are of general rather than specific application since the conductivity of any solution can be measured with this equipment if placed in a suitable cell. The preparation of the solutions, however, introduces problems peculiar to each individual solute, solvent and concentration. Consequently, the discussion in this section is concerned only with the method and accuracy of preparation of the 0.1 D KCl solution, which Jones and Bradshaw stated contains 7.41913 grams KCl per 1000 grams of solution, both weights corrected for air buoyancy; the weight of salt must be known to ± 0.05 mg. and the weight of the solution to ± 7 mg. in order that the concentration shall be accurate to ± 0.001%.

The requisite accuracy in weighing is attained by the use of a No. 10 Troemner balance for the salt and of a No. 00 Troemner balance for the solutions. The capacity of the No. 10 balance is 200 grams and that of the No. 00 balance is one kilogram. Although this latter figure is exceeded in weighing the solutions (the total weight on each pan being about 1.4 kilograms) the accuracy and sensitivity of the weighings is not appreciably impaired by the overloading. At least 1000 grams of solution should be prepared in order to permit check conductivity measurements and also to provide enough solution for rinsing the cells.

Both balances are provided with small pieces of porous plate impregnated with impure radium chloride in order to dissipate any electrostatic charges in the balance cases.

The weights consist of two sets of gold plated Class S brass weights one set ranging from 5 milligrams to 50 grams with a 5 milligram rider and the other ranging from 100 grams to 1 kilogram. This second set and a single one gram weight were tested and certified by the Bureau of Standards with sufficient accuracy.

All of the weights were intercompared by the Richards[68] method as modified by Weatherill.[88] The weights up to 50 grams were compared on the No. 10 balance. Successive determinations with the same combinations of weights agreed in all cases within less than ± 0.05 milligram. The weights from 100 grams to one kilogram were compared on the No. 00 balance and successive determinations with the same combinations agreed in all cases within ± 0.5 milligram. These variations are within the allowable limits and indicate that the mean values are known with more than sufficient accuracy. The values for the weights up to 50 grams were computed on the basis of the certified value of the 100 gram weight. As a check on these results, the single certified one gram weight was included in the comparisons. Its value as certified agrees within 0.03 milligram with the value calculated from the comparison data. The comparison of the weights from 100 grams to one kilogram agreed with the certified values within one milligram in all cases.

During the measurements with the No. 10 balance, it was found that the rider scale graduations are in error and are also incorrectly located on the beam. This was evidenced by the comparison of the rider with the 5 milligram weight. With the rider on the beam, it was apparently lighter than the 5 milligram weight by 0.006 milligram. With the rider on the pan, it was apparently heavier by 0.020 milligram, an obvious discrepancy. Further tests showed that the rest point with no loads on the pans and with the rider removed was not the same as when the rider was placed at the reading 0.0 on the beam, that is, in the center. Actually the true zero of the beam is at the left of the indicated zero by an amount corresponding to 0.03 milligram. The 5.0 milligram mark at the left end of the beam is too far to the right by 0.05 milligram on the beam scale. The 5.0

milligram mark at the right end is correctly located. When these errors were taken into consideration, it was found that the rider has a correction of + 0.023 milligram and the 5 milligram weight has a correction of + 0.003 milligram.

In the determination of the sensitivities for the various loadings and the translation of the deflection readings of the pointer into actual weighings, it is necessary to consider both the errors in the beam scale and the actual value of the rider. If R denotes the beam scale reading, it is corrected with sufficient accuracy for the scale errors by the addition of $\left(1 - \frac{R}{5}\right)0.03$ mg. if the setting is on the right side of the zero point or by the addition of $\left(1 + \frac{R}{5}\right)0.03$ mg. if it is on the left side. The correction for the rider value may be applied by multiplying the value of R as first corrected by 1.005. These correction were applied to all the comparison measurements up to 50 grams and are necessary to realize the degree of accuracy sought.

From the results of the comparisons of the weights it may be concluded that in so far as the knowledge of the values of the weights are concerned and the performance of the balances, the solutions may be prepared with an accuracy better than $\pm$ 0.001%.

The weighing of the solute and the solution.

It will be described later how the solute, which is in this case KCl, is prepared for weighing by fusion in a platinum-rhodium boat and then enclosed in a small narrow weighing bottle. A special weighing bottle of this type is known as a "piggy" and will be so referred to in the following discussion.

At this point it will be appropriate to discuss the precautions required and the errors involved in the determination of the weights of solute and solution. The buoyancy effect of the air on the piggy may be eliminated by using the tare and substitution method of weighing. In order to realize the desired accuracy in determining the weight of the KCl, the weight of the piggy and the tare must be the same within certain limits. The buoyancy effect of the air on Pyrex glass is about 0.05% of the weight of the glass. In order to eliminate any buoyancy correction for the glass, the buoyant effect on the difference in weight of the piggy and the tare must be less than the desired accuracy in weighings. This condition requires that the piggy and tare must agree in weight within 0.1 g. Actually an agreement within 0.02 g. is attainable.

A special flask was designed and built for the preparation and weighing of the solution on the No. 00 balance. It is illustrated by a line drawing in Figure 36. The neck is offset to permit placing the flask on the balance. The larger tube insealed to the neck is for a mercury seal in case it is necessary to stir the solution and still protect it from contamination by the atmosphere. A small aluminum table with brass legs and a corresponding counterpoise are placed on the balance pans and the flask rests on one of these. The tables are tall enough to permit placing the required weights on the pans. The auxiliary joint which fits into the neck of the flask permits direct connection to the siphon tube on the main receiver of the conductivity water still which will be described later. The water may be introduced directly into the flask without contacting the laboratory air as the flask may previously be swept out with purified dry air before the determination of its weight when empty.

In the preparation of a solution, the weight of the KCl to be used is first measured and then the weight of water may be calculated. The etch marks on the neck of the flask, after suitable calibrations are made, serve as reference points to indicate the approximate volume of water needed. The final adjustment of the amount of water is made by using the auxiliary joint as a dropper. The tip, t, is replaced by the tip, u, and the portion of the joint marked s is filled directly from the receiver on the still. The opening in u is small enough so that the joint may be disconnected from the receiver and capped with m before much of the water has discharged from the tip. The joint is put on the flask and the requisite number of drops of water are forced out by gently squeezing the piece of rubber tubing, r. The joint is removed, the cap A replaced and the weight determined. If more water is needed, the process may be repeated. The small tube leading to the bottom of the flask is used to make connection with the conductivity cells so the solution may be forced into them by air pressure applied through the auxiliary joint in the main neck.

The weight of the solution is found by the tare and substitution method. For this purpose a second similarly shaped flask was constructed. As in the case of the piggy, the weight of the flask and its tare must be the same within certain limits. If the solution is to be accurately weighed to ± 7 mg. without a buoyancy correction exceeding 0.05%, the differences in the weights of flask and tare cannot exceed 14 g. Actually an agreement was attained to within 1 g.

Treatment of the results of the weighings.

In comparing the various weights it is unnecessary to consider the buoyant effect of the air as the comparisons may be made sufficiently close together in time and the weights from 1 gram to 1 kilogram are all of brass. For the fractional weights, a table is provided in the Bureau of Standards Circular, "The Design and Test of Standards of Mass", giving the corrections to be applied to the aluminum fractions when they are assumed to have the density of brass weights. For the 500 mg. weight this correction amounts to -0.151 mg. and decreases with the magnitude of the weight. Variations in the density of the air will affect these values, but ordinarily the variations may be neglected since rarely will the uncertainty from this cause exceed 10% of the value of the reduction term. In weighing an object such as flask of solution, however, it is necessary to determine the buoyancy effects of the air displaced by the solution and by the weights. This may be accomplished by the method described in the Bureau of Standards Circular mentioned above. This procedure, which is universally used, involves a determination of the density of the air, the density of the object, the density of the weights and the apparent weight of the object in the air.

The density of the air may be found by determination of the temperature and pressure. The density of air as a function of temperature and pressure is tabulated in the Bureau of Standards Circular mentioned above. The temperatures of the No. 10 and No. 00 balance cases are determined in each case by two mercurial thermometers graduated in 0.2° and 0.1° intervals respectively. All of the thermometers are of ample accuracy since an error of 0.5° may be tolerated. The air pressure is found by a Fuess Kew pattern barometer hung near the balances. Readings to ± 0.1 mm. may be made, but ± 0.5 mm. is sufficient accuracy. For the reduction of the pressure observations to 0°C., sea level and 45° latitude, a number of comparisons were made with a more accurate barometer, a Green instrument which reads to ± 0.05 mm. and which was shown by comparison with the Normal Barometer to be accurate to 0.25 mm. The comparisons were made at a variety of pressures and temperatures. For readings from 725 to 745 mm. and at temperatures from 23 to 26°, a constant correction term of -4.4 mm. may be applied with sufficient accuracy to the Fuess instrument. In the calculation of the density of the air, the pressure must be corrected for the humidity. The appropriate correction term is found from the wet and dry bulb readings of a sling psychrometer by reference to the proper table in the Bureau of Standards Circular.

By the method just described, the density of the air in the balance cases may be found with sufficient accuracy so that buoyancy corrections may be applied to the weighings in order to obtain an accuracy of ± 0.05 mg. for the weighing of the KCl and ± 7 mg. for the weighing of the solution.

The weight of the KCl is found from four readings. First the piggy plus the boat on the left pan of the No. 10 balance are counterpoised with some ordinary analytical weights on the right pan. The piggy and boat are replaced by the tare and the requisite amount of calibrated weights. This amount is considered as that which is necessary to restore the former rest point. After the salt has been fused, the piggy plus the boat plus the KCl in the left pan are counterpoised by a new combination of weights on the right pan. The objects on the left pan are then replaced by the tare and a different amount of calibrated weights than were used before. The weight of the KCl in vacuo is equal to the effective value of the calibrated weights in the second case plus the buoyant force of the air on the salt plus the buoyant force of the air on the boat in the second case minus the effective value of the calibrated weights in the first case minus the buoyant force of the air on the boat in the first case.

The effective values of the weights are found by application of the calibration corrections to the nominal values and then subtraction of the buoyancy correction for the air displaced. This latter correction may be expressed as $\frac{M\rho}{8.39}$ where M is the value of the weights, ρ is the density of the air displaced and 8.39 is the density of the weights at room temperature.

The density of solid KCl at various temperatures is given in the International Critical

Tables.[27] The values needed in this work are: $d_4^{20} = 1.988$ g./cm.^{3}, $d_4^{25} = 1.987$ g./cm.^{3} and $d_4^{30} = 1.986$ g./cm.^{3}. The buoyancy correction of $\frac{M\rho}{d_4^t}$ may be calculated where M is the apparent weight of KCl, ρ is again the density of the air and d_4^t is the density of solid KCl at temperature t.

The density of the platinum-rhodium alloy of which the boat is constructed was not found in the literature. However, the error in assuming that its density is the same as that of platinum is negligible since only the difference in the buoyancy effects in the two cases is involved rather than the total correction. The combined buoyancy correction is $\frac{M(\rho_2-\rho_1)}{21.4}$ where M is the apparent weight of the boat, ρ_2 and ρ_1 are the two values for the air density and 21.4 corresponds to the density of platinum.

The weight of solution is likewise found from four readings. First, the flask plus the boat plus the salt on the left pan are counterpoised by ordinary analytical weights on the right pan. Next the tare and requisite amounts of calibrated weights are substituted on the left pan. After adding the water and producing a homogeneous solution by bubbling air through the flask in a manner to be described later, the flask plus the solution plus the boat are counterpoised by analytical weights on the right pan. Finally, the tare and another combination of calibrated weights are substituted on the left pan. The weight in vacuo of the water added is equal to the effective value of the calibrated weights in the second case plus the buoyant force of the air on the solution plus the buoyant force of the air on the boat in the second case minus the effective value of the calibrated weights in the first case minus the buoyant effect on the solid salt minus the buoyant effect on the boat in the first case. As in weighing the salt, the effective values of the weights are found by applying the calibration corrections to the nominal values and subtracting the buoyant forces of the air. The buoyant forces on the salt and the boat are found as described above under the weighing of the salt. The density of the solution is needed to ascertain the buoyancy correction on it. Parker and Parker[64] determined the density of 0.1D KCl at 0° as 1.004887 g./cm.^{3} The values at room temperature may be determined with sufficient accuracy by the assumption of the same temperature coefficient for the 0.1 D solution as for that indicated for 1 and 2% solutions by values given in the International Critical Tables.[28]

The values calculated are 1.0030 g./cm.^{3} at 20°, 1.0018 g./cm.^{3} at 25° and 1.0004 g./cm.^{3} at 30°. These values are probably accurate to within $\pm$ 0.05% whereas the buoyancy correction may be found with sufficient accuracy if they are in error by $\pm$ 5%. The buoyant force of the air on the solution is expressible as $\frac{M\rho}{D_t}$ where M is the observed weight, ρ is the density of air displaced and D_t is the density of the solution at the temperature of the balance case.

By the treatment described above, the results obtained represent the weights in vacuo of the salt and water in each case with sufficient accuracy so that the error in the final conductivity value for 0.1 KCl due to errors in weighings will not be more than $\pm$ 0.001%.

Proof of the accuracy of weighing.

As verification of the above contention that the salt and the water may be weighed with sufficient accuracy, a number of tests under a variety of conditions were conducted.

The precision attainable in weighing with the No. 10 balance is indicated by a series of five determinations on a 15 g. weighing bottle. These results were obtained over several days and the appropriate buoyancy corrections were applied. The average deviation was $\pm$ 0.02 mg. These results indicate that reproducible results well within the allowable limits of accuracy may be realized with the No. 10 balance.

A series of weighings on the empty solution flask were made to ascertain if its weight can be reproducibly determined. Three successive weighings agreed within $\pm$ 1 mg. After each weighing the various ground joints were taken apart and put together in simulation of the manipulations actually followed in preparing a solution and adjusting the amount of water. The flask was filled with water and weighed. The stopper was removed for fifteen minutes and a loss of weight of 2 mg. was noted. Again the stopper was removed, this time for seventeen minutes, and a further loss of 8 mg. was detected. Although the losses do not correlate with the time of exposure, the performance is satisfactory. The time of exposure was considerably greater than any that would be experienced after the solution had been finally weighed and made ready for transfer to the conductivity cells. The losses found are of the order of

magnitude of the necessary accuracy in weighing of the solution.

In the preparation of the solution and in the transfer of it to the conductivity cells, a supply of purified air under pressure is needed. It is used to stir the solution and also to force the solution from the flask. The supply of purified air is obtained by passing compressed air through anhydrous $CaCl_2$, soda and lime, absorbent cotton, concentrated H_2SO_4, ascarite, absorbent cotton and finally two wash bottles with sintered glass membranes which produce fine bubbles. The two bottles are filled with conductivity water. In dealing with a KCl solution, this water should be replaced by solution of the same concentration. To determine whether the contact of this air with the solution results in a loss of weight, a slow stream of air was bubbled through a liter of water for forty-five minutes. The loss in weight was only 2 mg.

These tests indicate that the solutions may be prepared with the requisite accuracy from the standpoint of their composition by weight.

The Preparation of the Conductivity Water.

From the standpoint of the accuracy in the conductivity values to be obtained, other factors than the various weights of materials must be taken into consideration regarding the solutions. The water used in the preparation of the solutions will itself have a conductivity which must be determined. Even if the water is carefully purified, in the case of a 0.1 D KCl solution its conductivity may constitute 0.005% to 0.010% of the total. A neglect of this factor would introduce a serious error into the desired values. The amount of impurity in the water must be minimized also in order to avoid any possibility of reaction between the solute added and the impurity in the water.

The purification is accomplished by the redistillation of the distilled water supplied to the laboratory. The still used for this purpose and pictured in Figure 37 is patterned after the type designed by Kraus and Dexter.[49] A separation of the more volatile components of the distillate is accomplished and only the middle fraction of the purer portion of condensate is collected in the main receiver. This consists of a thoroughly seasoned 24 l. Pyrex flask fitted with a ground glass stopper with a mercury seal. The stopper is suitably connected to the bottom of the block tin condenser which delivers the better quality water without contact with the laboratory atmosphere. A three way mercury seal stopcock is interposed between the condenser and the flask to permit rejection of the first and last fractions into an auxiliary receiver. A siphon tube with mercury seal stopcock permits removal of the collected water as desired. The air in the receiver is expelled during collection of the water through a guard bottle containing 50% NaOH solution. When water is removed from the flask, the air which enters is purified by successive passage over anhydrous $CaCl_2$, soda and lime, ascarite and absorbent cotton. It finally bubbles through water to indicate the rate of flow. This wash bottle with water also insures expulsion of the moist exhausting air through the NaOH solution and not through the dry absorbing reagents. The auxiliary receiver is similarly protected.

To operate the still, the 60 l. copper tank is filled with distilled water and a charge consisting of 35 g. of $KMnO_4$ and 50 g. of $NaOH.H_2O$ crystals of low CO_3 content is added. Five Meker burners are employed for the distillation. One of these is lighted and the solution allowed to digest overnight to oxidize any organic matter and liberate any NH_3 present. In the morning the other burners are turned on and in an hour the distillation is proceeding steadily. After about 10 l. have been collected in the auxiliary receiver, the flow is divided so that the purer water flows into the main receiver. The distillation is continued for four to six hours during which time 8 to 12 l. of the purer water are collected. The back pressure in the guard bottles is regulated so that about four-fifths of the total distillate during this period is collected in the main receiver and the remainder in the auxiliary receiver. When a sufficient quantity has been collected, the flow is again directed to the auxiliary receiver and the burners turned off. Occasionally the still is emptied, rinsed and a fresh charge of reagents added. One charge may be used for at least three distillations and possibly more although in practice the still was emptied completely about every third time.

Tests of the conductivity of the water taken directly from the main receiver without exposure to the air indicated values between 0.3 and 0.5 $\cdot 10^{-6}$ $ohm^{-1}cm.^{-1}$ at 25.0°. These values represent from 0.002 to 0.004% of the conductivity of a 0.1 D KCl solution at 25°.

The Determination of the Conductivity of the Water.

The conductivity cell and its calibration.

It is of course impossible to determine directly the effective contribution of the water to the conductivity of the KCl solution. Since it is very small, however, a sufficiently accurate method is to measure the conductivity of the water before any salt is added and demonstrate that its conductivity does not change by an appreciable amount when carried through the various manipulations made on the solution, but in the absence of the KCl. The conductivity cell for the measurements of the water was designed and constructed according to the principles of cell design laid down by Jones and Bollinger.[34] From its photograph in Figure 38, it may be seen that the parts of opposite polarity are as widely separated as possible. Corning Normal glass was used since it has nearly the same coefficient of expansion as platinum and the arms of the electrodes may therefore be sealed through to permit electrical contact. The platinum electrodes are 50 mm. in diameter and approximately 1.5 mm. apart. They were given a light deposit of platinum black to diminish the effects of polarization. The cell may be immersed in the large oil thermostat so that the body of the cell is about 10 cm. below the surface.

The cell constant was found at 25.00° ± 0.02°C. by measurements with 0.01 D KCl prepared by weight methods. The resistance when filled with this solution is about 8 ohms. Since this can only be measured to 0.01 ohm with the alternating current bridge the cell constant cannot be determined with an accuracy greater than ± 0.1%. The accuracy could be improved if a solution of lower concentration were used, but such a determination is unnecessary. An error of nearly 20% in the conductivity of the water used in preparing the 0.1 D solution may be permitted and still affect the final value by only 0.001%.

The cell constant determinations were made with current frequencies of 696, 1096 and 1865 cycles per second. Variations of resistance with frequency of as much as 0.1% were detected. Two preparations of solution and two fillings with each were used. The values at 696 cycles did not agree as well as those at the higher frequencies, differences of ± 0.1% being detected. The data was treated by the method recently developed by Jones and Christian[37] which yields the resistance at infinite frequency when polarization would be completely absent. The cell constant as determined in this manner is 0.01159 ± 0.00002 $cm.^{-1}$ If only the results at 696 cycles had been used, an error of 0.2% due to polarization would have been introduced.

One arm of the cell was broken off about a month later. After the repairs had been made, the cell constant was redetermined. Three preparations of solution and two fillings from each were used and the same value was obtained, namely 0.01159 $cm.^{-1}$. This value is probably accurate to ± 0.1%, the results being more concordant than at the first calibration. As pointed out above this error is entirely negligible.

An important point in technique was disclosed in this second determination. The electrical contact to the alternating current bridge is made by means of two copper rods which dip into the side arms of the cell, these arms are partially filled with mercury. If appreciable amalgam is formed as evidenced by the fouling of the mercury, poor contact is obtained with the platinum rods leading to the electrodes. The remedy of course is to change the mercury and clean the side arms.

It was found that a protracted rinsing treatment of the cell extending over several months was necessary in order to render it fit for measurements on the conductivity water. An appreciable quantity of KCl had evidently been adsorbed in the cell, probably on the platinum black. When finally leached out and filled with high quality water, the resistance could readily be measured to ± 5 ohms in 25000 ohms, or with a precision of ± 0.02%.

Tests on the water for solutions.

By the use of the cell described above, tests were performed on the water. A sample was collected in the flask for the preparation of solutions and carried through all the steps which would normally be followed except that no KCl was added. After this treatment its conductivity was $0.39 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25.0° whereas a sample collected directly from the receiver at the still into the conductivity cell had a conductivity of $0.34 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25.0°. This indicates a negligible change on handling.

In the above case the purified air was bubbled through the water for 15 minutes. To ascertain if excessive bubbling would cause an appreciable conductivity change, the passage of air was continued for

nine hours and the conductivity was $0.18 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25.0°. Since this change is greater than can be tolerated in terms of the final conductivity values, excessive bubbling must be avoided.

To determine the amount of electrolyte acquired by prolonged contact with the atmosphere, another sample with an initial conductivity of $0.56 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25.0° was exposed for 45 minutes, the stopper of the flask being removed. The conductivity increased to $0.63 \cdot 10^{-6} ohm^{-1} cm.^{-1}$ at 25.0°. This change is of the same order of magnitude as the allowable error from the point of view of the 0.1 D KCl and is therefore too great. However, as indicated under the experiments on weighing the solution, such a length of exposure is far in excess of any experienced in practice.

These tests serve to indicate the precautions to be taken in the preparation of the solutions. The solution should not be exposed to the atmosphere for more than fifteen minutes unless a stream of purified and saturated air is used to steadily sweep out the neck of the flask. The bubbling of the air should not be continued for more than 30 or 45 minutes as excessive bubbling changes the conductivity just as much as excessive exposure, but in the opposite sense. It is evident that if these precautions are observed, the measurements of the conductivity of the water as separately determined represents the conductivity of the water in the solution with an accuracy in terms of the final conductivity values of approximately $\pm$ 0.0005%.

The Purification of the Potassium Chloride.

Introduction.

Another factor which must be considered in the preparation of the solutions is the purity of the solute. The amount of contaminating material must not be sufficient to cause an error of 0.001% in the measured conductivity. The amount of impurity which may be tolerated will vary, therefore, depending on the nature of the material. If it is non-electrolytic in character, the amount will be represented by 0.001% of the weight of the solute. For 0.1 D KCl this is 0.07 mg. per 1000 g. of solution. However, if the impurity is electrolytic, the conductivity of the impurity must be considered. The chief impurities in KCl according to Jones and Bradshaw are Mg and SO_4. They found that repeated recrystallizations gave a product freed of these radicals as evidenced by qualitative tests. As much as 0.14 mg. of $MgSO_4$ per 1000 g. of solution could be present in the material which was supposedly all KCl without affecting the conductivity by more than 0.001% since the $MgSO_4$ will assist in the conduction of the current, although to a different degree. The most satisfactory criterion of purity of solute is the agreement in conductivity values obtained between samples from different manufacturers and purified by different methods.

Chemical purification.

Five samples were prepared using materials from different sources and employing various procedures. For sample A the starting material was 1.5 kg. of Merck C. P. KCl. This was dissolved in sufficient conductivity water in Pyrex beakers and filtered by suction through a Büchner funnel with a hard filter paper to remove foreign matter. After slow boiling of the solution on an electric hotplate until saturated, it was removed, packed in ice and salt and stirred at intervals. The product was centrifuged in platinum vessels and then washed twice by making a sludge each time with conductivity water and centrifuging. This process reduces the yield very materially as the solubility of the KCl is appreciable at room temperature. The recrystallization process was carried out four times in Pyrex vessels. Before the last time the solution was filtered through a clean porcelain bottom filtering crucible. Twenty-six grams of product were obtained. Recrystallization in this fashion with washing each time is much more rapid than an extended series of recrystallizations without washing and is probably as effective in removing impurities.

Sample B was prepared from about 1 kg. of J. T. Baker C. P. KCl. This was treated in similar fashion to sample A but was recrystallized only three times. The yield was 46 g.

Sample C was prepared from 1 kg. of Mallinckrodt Reagent Quality KCl. After dissolving in sufficient water, the solution was filtered similarly to samples A and B. A surprising amount of foreign matter was present for so-called Reagent Quality material. The salt was recrystallized, centrifuged and washed twice with centrifuging each time. It was then dissolved and heated until nearly saturated at 90°C. HCl gas was introduced

through an inverted funnel which was part of an all glass HCl generator. The gas was obtained by warming doubly redistilled HCl. This distillation was carried out in the presence of a small amount of $KMnO_4$ in an all glass apparatus as recommended by Archibald.[1a] The first quarter of the distillate was rejected and the middle half collected. This was redistilled in the same way and only the middle half collected for use in the generator. The introduction of the HCl caused an appreciable quantity of the KCl to precipitate. The generator was removed and the suspension packed in ice and salt to induce further crystallization. The product was centrifuged and washed twice with centrifuging each time. It was then recrystallized twice with the customary centrifuging, washing and filtration before the last recrystallization. Nineteen and one-half grams of product were obtained.

Sample D was prepared from 1 kg. of Mallinckrodt Reagent Quality KCl. It was treated like Sample C being recrystallized once. An attempt to salt out with HCl gas prepared from doubly redistilled HCl failed due to excessive dilution by the water which carried over with the HCl gas. The solution was boiled until saturated, then cooled in ice and salt and centrifuged without washing. The KCl was then dissolved to prepare a solution saturated at room temperature. It was salted out with HCl prepared by adding redistilled H_2SO_4 drop to doubly redistilled HCl in the gas generator. A good yield of KCl was obtained. The sludge was centrifuged without previous cooling and the product was not washed. It was then dissolved, filtered through the porcelain bottom filtering crucible and recrystallized once, centrifuged, but not washed. The yield was 42.5 g.

Sample E was accidentally contaminated with some iron and so was rejected.

Sample F was prepared in identically the same manner as sample A except that the washing of the salt was omitted. A yield of 40 g. was obtained from 700 g. of starting material which was from the same manufacturer's lot as sample A.

Purification by fusion.

All of the salt preparations are snow white in appearance, but undoubtedly they contain impurity in the form of occluded water and in the case of samples C and D possibly some HCl. The only way in which these materials can be removed is by fusion. The salt should be fused in dry nitrogen in order to avoid attack on the platinum boat and excessive hydrolysis. Johnson[31] has recently shown that carefully purified KCl may be fused in a current of dry nitrogen with only one or two parts of alkali produced per million parts of salt. Further hydrolysis may occur, but in the vapor phase and hence will not affect the final product. The effect of this alkali on the conductivity value for 0.1 D KCl may be calculated. If 0.0002%, or two parts in a million, of the amount of KCl required to make a 0.1 D solution is replaced by KOH formed by hydrolysis, then a correction may be applied by subtraction from the conductivity of the 0.1 D KCl solution the conductivity of the KCl replaced by KOH and by the addition of the conductivity due to the KOH present. The net result is an increase of 0.00035% in the conductivity over the value obtained if the material were entirely KCl. This source of error could probably be eliminated by carrying out the fusion in an atmosphere of dry HCl gas. The apparatus as at present assembled is for fusion in nitrogen.

In order to avoid any acquisition of water after the fusion and while cooling, arrangements are provided to handle the fused salt in a Richards[69] bottling apparatus. The set up as made for fusion in nitrogen is shown diagrammatically in Figure 39. The combustion tube is of Corning 172 glass tubing which will withstand the necessary heating without appreciable softening. The remainder of the apparatus is constructed of Pyrex glass.

The nitrogen obtained from a cylinder is purified by passage over the appropriate reagents. The gas first passes through a wash bottle containing a small amount of concentrated H_2SO_4 to indicate the rate of inflow of the gas. It next passes a combined pressure regulator and safety valve, thence to a combustion tube of Corning 172 tubing containing hot CuO to oxidize any organic matter. The products of this combustion are absorbed in soda and lime. Another combustion tube containing copper turnings in a spongy mass heated to about 550° is next inserted for the removal of any oxygen in the nitrogen. Two towers filled with glass beads wet with 50% KOH for removal of CO_2 and two similar towers with beads wet with concentrated H_2SO_4 for removal of NH_3 finally lead the gas to a tube of dehydrite for removal of the last traces of H_2O and thence to the bottling apparatus and the combustion tube for the fusion. The outlet is protected by a small drying tube containing dehydrite with an arm dipping into concentrated H_2SO_4 to indicate the rate of outflow of the gas. Glass grids are suitably placed to give flexibility between the various parts

of the train which are connected by ground glass joints. The current in the heater for the fusion may be gradually increased so that melting occurs about three hours after the start. Some volatilization of the salt takes place with subsequent deposition on the wall of the tube in the cooler region. Johnson[31] has found that on fusion of 7 g. of carefully purified KCl the weight decreased between 2.8 and 9.0 mg. This volatilization makes it necessary to weigh the sample of KCl after the fusion rather than before. The weighed sample is then introduced into the flask and the required amount of water is added.

After the salt has partially cooled, the nitrogen is replaced by dry air which is purified in a second train. The pressure is created by an aspirator bottle which delivers the air past a combination pressure regulator and safety valve to a wash bottle containing concentrated H_2SO_4 and a tower of anhydrous $CaCl_2$ to remove most of the water vapor and spray. The H_2SO_4 bottle also serves to indicate the rate of inflow of the air. The air is next passed through a tube containing hot CuO to oxidize any organic matter, the products being absorbed in soda and lime. The air is then scrubbed by two towers with 50% KOH and two towers with concentrated H_2SO_4 similar to those in the nitrogen train. It is connected with the nitrogen line by a three-way stopcock where it passes on into the dehydrite, bottling apparatus, combustion tube and outlet. When the bottling apparatus is full of dry air and the salt has cooled nearly to room temperature, the boat with the fused salt is pushed into the piggy and the stopper manipulated into place.

It is necessary of course to first determine the weight of the empty boat and the piggy as tared before the KCl is added and fused. The platinum-rhodium boat easily contains the requisite 7.4 g. of KCl both before and after fusion.

Conclusion.

The accuracy of the final conductivity values as influenced by the solutions themselves may be determined by considering separately the errors due to the solute and the solvent.

After taking into consideration the calibration of the weights, the precision of weighing the salt, the hydrolysis on fusion and the various buoyancy corrections, the uncertainty in the final conductivity value introduced by the KCl may be expressed as about $\pm$ 0.001% when fusion is carried out in nitrogen.

So far as the solvent is concerned, the errors involved relate to the calibration of the weights, the precision of weighing the solution, the changes in the conductivity of the water, the measurement of the conductivity of the water and the various buoyancy corrections. The magnitude of the combined uncertainty from these sources is about $\pm$ 0.0015% in terms of the final conductivity values.

The net error to be expected in the conductivity value for 0.1 D KCl from these sources would therefore be $\pm$ 0.0018%.

THE METHOD FOR THE STANDARD VALUE CONDUCTIVITY DETERMINATIONS

THEORY OF DESIGN OF THE CELLS.

Introduction.

The simple relation between resistance and conductivity,

$$K = \frac{1}{R} \cdot \frac{L}{A}$$

holds only provided both L and A are uniform throughout the cell. If, however, the cell is irregular in shape, as is usually the case, it is necessary to mathematically divide it into a series of segments of length ΔL and corresponding cross sectional areas $A_1, A_2, \ldots A_n$. The value of ΔL is made sufficiently small so that the values of the areas are essentially constant for each segment. Then the conductivity is expressed as

$$K = \frac{1}{R_1} \cdot \frac{\Delta L}{A_1} = \frac{1}{R_2} \cdot \frac{\Delta L}{A_2} = \ldots \frac{1}{R_n} \cdot \frac{\Delta L}{A_n}$$

where $R_1, R_2, \ldots R_n$ are the resistance of the corresponding segments. By a transposition of terms, a series of equations is obtained,

$$R_1 = \frac{1}{K} \cdot \frac{\Delta L}{A_1},$$

$$R_2 = \frac{1}{K} \cdot \frac{\Delta L}{A_2},$$

$$\vdots$$

$$R_n = \frac{1}{K} \cdot \frac{\Delta L}{A_n}.$$

By summation

$$R_1 + R_2 + \ldots R_n = \frac{1}{K} \Sigma_1^n \frac{\Delta L}{A_1} \ldots \frac{\Delta L}{A_n}.$$

However, $R_1 + R_2 + \ldots R_n = R$, the total resistance of the conductor. Therefore

$$R = \frac{1}{K} \Sigma_1^n \frac{\Delta L}{A_1} \ldots \frac{\Delta L}{A_n}$$

$$\text{or} \quad K = \frac{1}{R} \Sigma_1^n \frac{\Delta L}{A_1} \ldots \frac{\Delta L}{A_n}.$$

The term $\Sigma_1^n \frac{\Delta L}{A_1} \ldots \frac{\Delta L}{A_n}$ is the dimension factor and is called the "cell constant" when dealing with an electrode vessel for use with electrolytic solutions.

In the present work the objective has been to maintain such uniformity in the dimensions of the cell that the term

$$\Sigma_1^n \frac{\Delta L}{A_1} \ldots \frac{\Delta L}{A_n}$$

becomes equal to L/A, so that the relation between resistance and conductivity reduces to the simple form

$$K = \frac{1}{R} \cdot \frac{L}{A}.$$

It was indicated after the analysis of the work of Parker and Parker[64] and of Jones and Bradshaw[36] on the determination of standard reference values, that it is the purpose of this work to redetermine those values with an accuracy at least equal to that attained by Jones and Bradshaw, but by the use of cells similar in principle of design to those of Parker and Parker. In other words the cells are to consist of straight, cylindrical glass tubes of uniform bore and their cell constants are to be found by direct measurements of the lengths and cross sectional areas. The choice of dimensions is governed by a consideration of the accuracy to be obtained in the resistance measurements and in the cell constant determinations. The most satisfactory way to select the dimensions of the cells is to consider first, the resistance measurements and second, the accuracy needed in the cell constant determinations.

The Analysis by Washburn.

In 1916 Washburn[86] published a classical treatise on the design of conductivity cells, based on the accuracy of the resistance

determinations and the control of the temperature of the conductivity cells. The bridge network for the resistance measurements is taken as the starting point in the analysis. It is composed of the conductivity cell in one arm, considered with its lead wires as a resistance shunted by a condenser, a measuring resistance shunted by a variable air condenser in an adjacent arm and a slide wire to comprise the remaining two arms. The detecting device for the determination of the balance point is the telephone receiver. The distribution of current may be considered for an unbalanced bridge. By the application of Kirchoff's Laws Washburn found that the total current may be expressed as

$$I = \frac{I_T}{2\Delta R_B}\left[\frac{(\frac{R_B}{2} + Z)^2 + 2\,R_T\,(\frac{R_B}{2} + Z)}{Z}\right]$$

where I is the total current, I_T is the audibility current of the telephones which may just be detected when the slide wire contact is moved from the balance position by an amount ΔR_B. The total resistance of the slide wire is R_B, and Z is the impedance of the cell and of the adjacent arm. The symbol R_T represents the resistance of the telephones. He determined that the active component of this current can be expressed approximately as

$$I = \frac{I_T}{2\Delta R_B R}\left[(\frac{R_B}{2} + R)^2 + 2\,R_T\,(\frac{R_B}{2} + R)\right]$$

where R represents the resistance of the conductivity cell. The uncertainty in ΔR_B affects the measured value of resistance of the cell. Washburn conservatively considered that $2\Delta R_B$, the total range of no sound, is equal to

$$\frac{pR_B}{100}$$

where p is the percentage error in the measured resistance.

When the current flows through the cell, heating of the solution results. Washburn made another conservative assumption that none of this heat escapes, but is all used in raising the temperature of the solution. The temperature rise depends upon the volume, the density and the specific heat of the solution, the time required to make the bridge setting and the current passing through the cell. The effect of a temperature rise, ΔT, on the conductivity may be expressed as $p_t = 100\alpha\Delta T$ where p_t is the resulting percentage error in the conductivity and α is the temperature coefficient of conductivity of the solution.

On the assumption that the error due to temperature rise and the error in bridge setting are to be equal, Washburn obtained an expression for the minimum allowable area of the electrodes. He considered the cell to consist of two parallel electrodes, L cm. apart and contained in a vessel of uniform cross sectional area A $cm.^2$, which he also considered as the area of each electrode. The expression for the minimum area is

$$A \geq \frac{50\,I_T\left[\frac{R_B}{2} + R + 2\,R_T\right]\sqrt{t}}{R\sqrt{K}\sqrt{\frac{0.042p^3\,ds}{\pi}}}.$$

The terms of this equation which have not been defined as yet are t, the time required to make the setting of the bridge, K, the conductivity of the solution, d, the density and s, the specific heat of the solution. The value of L may be computed from the equation

$$L = R\,A\,K.$$

Washburn elaborated these results in order to apply them to the design of cells to cover various ranges of conductivities, the percentage accuracy of the measurements being governed by the fluctuations in temperature of the constant temperature bath. For the design of a cell to be used for a single solution, the equations given above are adequate. They are not directly applicable to the present case, however, because the bridge network is unlike Washburn's as is evidenced by reference to the description of the alternating current Wheatstone bridge. The method of analysis as developed by Washburn may be applied in principle, however.

The Adaptation of the Washburn Analysis. The alternating current Wheatstone bridge circuit with the cell in place as shown in Figure 2 may be considered with respect to the distribution of the current. The symbol I may be used to denote the total current from the oscillator which divides so that I_A passes through the arm containing the cell and I_B throughout the ratio coil R_4. If the bridge is unbalanced by changing resistance R, by an amount ΔR, current will flow in the primary of the input transformer of the amplifier. This current may be denoted by I_T. In order to simplify the analysis the following assumptions are made: (1) at balance the impedance of the cell arm of the bridge is equal to that of the adjacent arm containing R_2 and C_2; (2) R_3 and R_4 are essentially free of inductance

and capacitance and are also equal; (3) the impedance of the arms of the Wagner ground containing R_5 and R_6 are equal to each other and to the resistance of arms R_3 and R_4. This is obviously untrue, because of the presence of the condenser C_3, but the error in the final conclusions from such an assumption is inconsequential. On the basis of this last assumption the current in the Wagner ground arms is also approximately equal to the current in the arms containing the ratio coils. It is also assumed that when R_1 is changed by an amount ΔR in order to unbalance the bridge, the impedance of that arm becomes equal to $Z \pm \Delta R$. This is not rigorously true, but it is sufficiently exact for the case at hand.

On the basis of these assumptions and by applying Kirchoff's Laws regarding the flow of currents, an expression for the total current may be obtained which is similar in form to the Washburn equation and may be written as

$$I = \frac{I_T}{R \Delta R}\left[(2Z + R)^2 + 2Z_T(2Z + R)\right]$$

where Z denotes the impedance of the arm containing the cell, R corresponds to the resistance of R_3 and R_4, and Z_T represents the impedance offered by the amplifier to the current I_T. The current I is also approximately equal to

$$I_A\left(\frac{2Z + R}{R}\right).$$

If the error in the bridge setting expressed as p% is considered equal to $\frac{\Delta R}{Z}$, substitution for the values of ΔR and I yields the expression

$$I_A\left(\frac{2Z + R}{R}\right) = \frac{I_T 100}{R Z p}\left[(2Z + R)^2 + 2Z_T(2Z + R)\right]$$

which may be simplified to

$$I_A = \frac{100 I_T}{Z p}\left[(2Z + 2Z_T + R)\right].$$

In regard to the heating effect of the current I_A on the resistance of the cell, the relation derived by Washburn for this effect may be used directly, namely,

$$\frac{4.2 \, AL dsp_t}{100} = I_A^2 \frac{Lt}{AK}$$

where the various symbols have the meanings previously defined. If the percentage error in the conductivity due to the heating effect of the current is not to be greater than the percentage error caused by the uncertainty in the resistance measurement, p may be substituted for p_t and I_A eliminated between the last two equations. The resulting equation may be solved for A, thus,

$$A \geq \frac{100 I_T\left[2Z + 2Z_T + R\right]\sqrt{t}}{R\sqrt{K}\sqrt{\frac{0.042 \, dsp^3}{\alpha}}}.$$

A comparison of this equation with the corresponding one obtained by Washburn indicates the general similarity in form which is to be anticipated. The relation between L and A is the same as given by Washburn, namely,

$$L = ZAK.$$

In order to use the equation for A, an evaluation of the various terms must be made. The value of I_T may be found from the equation

$$I_T = \frac{I R \Delta R}{(2Z + R)^2 + 2Z_T(2Z + R)}.$$

in which R and Z may be reasonably assumed to each have a value of 1000 ohms and ΔR may be expressed as 0.01 ohm. With the measuring apparatus available it was difficult to estimate Z_T accurately, but a value of 2000 ohms may be selected as being approximately equal to the actual value at either 1000 or 2000 cycles. It was found by trial that when the value of I is 0.003 ampere, the bridge can very readily be balanced within $\pm$ 0.01 ohm for R_1 equal to 1000 ohms. The value of I_T as computed is then $1.4 \cdot 10^{-9}$ amp. This value of I_T does not represent the smallest possible current passing through the primary winding of the input transformer of the amplifier which would result in an audible sound in the telephones. It corresponds, instead, to the smallest convenient current for measurements with an accuracy of 0.001% made by a single individual. It will vary for different individuals depending on their powers of concentration in adjusting the bridge at

balance and on their keenness of hearing. Another value required in the equation for A is that for t which experience has shown may be given as 30 seconds. The value for the conductivity of 0.1 D KCl solution is about 0.01286 ohm^{-1} $cm.^{-1}$ at 25°. The product ds may be assumed equal to unity. In this work p has been chosen as 0.001%. The value of α for 0.1D KCl at 25° is 2% per degree. By substitution of these various values in the equation for A, it is found that the minimum allowable cross sectional area is 1.03 $cm.^2$. The corresponding value of the length of the cell, L, is 13.3 cm.

It is now necessary to reconsider the values for L and A in view of the assigned accuracy of 0.001% with which they have to be determined. The proposed plan for the determination of the cell constants will be discussed in detail below, but it has already been intimated that the evaluation of the lengths of the cells is to be accomplished by the use of the cathetometer and meter bar assembly. The limit of accuracy of length measurements with this equipment is 0.003 mm. which is the accuracy of certification of the meter bar by the Bureau of Standards. Now 0.003 mm. is 0.002% of 13.3 cm. so that the uncertainty in the determination of the cell lengths would be greater than desired. The situation can obviously be improved by selecting a larger value of L and correspondingly larger value of A. This would be satisfactory since the value of 1.03 $cm.^2$ for A is the minimum allowable. The value of L should be at least 30 cm. in order to measure it accurately to 0.001%. The corresponding value of A would be 2.34 $cm.^2$. This would correspond to a diameter of 1.72 cm.

On the basis of the values obtained in this complete analysis, a number of cells have been designed and prepared as will be described below.

THE PREPARATION OF THE CELLS.

The Glass Tubes.

The starting point in the actual development of the cells is the glass tubes. The selection of glass tubing which is uniform in internal cross sectional area within ± 0.001% from either hand or machine drawn commercial stocks is an impossible task.

Parker and Parker[64] lapped the insides of their cells by grinding and then polishing with rouge. Dr. Parker has indicated in personal correspondence that the lapping was done on a closely fitting steel rod rotated in a lathe. The glass tube was turned by hand in the opposite direction to the rotation of the rod. The grinding material was fine carborundum wet with water. On the basis of experience with an even more refined method of grinding similar tubing, which is described below, it seems very doubtful if such a method produced tubing of accurately uniform bore. Parker and Parker did not perform any tests to determine the actual degree of uniformity.

The most uniform bore tubing available on the market is the KPG tubing made by the Jena Glass Works in Germany. The method of fabrication was protected by a United States patent until April 22, 1936, the expiration date. By this, the Kueppers[51] process, the glass is softened and formed around a suitable mandrel so that it assumes the shape of the latter. The glass and mandrel separate on cooling so that the mandrel may be removed. Thus it is possible to convert ordinary glass tubing into precision bore tubing by subjecting it to this treatment using an accurately prepared mandrel.

The Jena Glass Works can furnish KPG tubing of varying degrees of exactness in dimensions. A supply of tubing of two different diameters in different lengths was obtained. The diameters were claimed to be 15.04 ± 0.01 mm. and 22.00 ± 0.02 mm. The lengths selected were such as to give cell resistances ranging from 700 to 1200 ohms. Before the tubes could be used as conductivity cells or calibrated, it was necessary to regrind the ends until they were plane and also perpendicular to the tube axes. The process used requires that the tubes be warmed to 150 to 200°. The glass was Durobax which is comparable to Pyrex in properties, but apparently it had not been satisfactorily annealed, for a number of tubes cracked while warming them very carefully. In addition, certain operations employed in the grinding of the ends disclosed that the tubes supposedly of one diameter did not agree among themselves by amounts ranging from 0.03 to 0.05 mm. and in some cases individual tubes varied by 0.03 mm. from one end to the other. It was evident

that the KPG tubing would not be satisfactory because of the existence of strains in the glass and because of the variations in diameter which were considerably in excess of the manufacturer's specifications.

The Kuepper's process was studied and developed so that a supply of tubes made from specially selected Pyrex tubing was prepared for this work. It was found that the operating description given in the patent is not sufficiently specific. In this process a mandrel of "any desired material" is placed inside the tubing which is then more or less evacuated and sealed off. The glass is heated to a "red heat" until it softens and conforms to the shape of the mandrel by virtue of the force of the atmosphere or other external agencies upon it. The temperature defined as a "red heat" is vague and indefinite. Also, no indication is given as to the nature of "any desired material" which can be used. It was decided to try a steel rod as the mandrel. Upon heating the glass until it softened and then slowly cooling, it was found that the glass and steel tended to adhere strongly in places so that the strains of contraction finally shattered the glass. After discussing these difficulties with the Corning Glass Works, they suggested that a temperature of approximately 750° might yield satisfactory results. According to them, the glass and metal stick together if heated to too high a temperature. This explains the failures experienced as in some cases the temperature reached as high as 850°. A further study disclosed that the temperature range for successful operation is critical. With the use of a tool steel rod of about 1.2% carbon content it was found that if the glass and rod are held at 650° for several hours, the shrinking is only partially complete. If the temperature is raised to 700°, the shrinking is essentially complete within an hour. If the temperature is raised to 750°, the glass invariably adheres to the steel rod and fracture results on cooling. It is essential then to control the temperature very carefully, a fact which is not brought out in the description of the patent.

An electric furnace was constructed for the preparation of the tubes. It consists of an alundum cylinder 7.5 cm. in internal cylinder and 47 cm. in length. The outside is wound with chromel ribbon, the turns being evenly spread. The winding was coated with alundum cement and an auxiliary winding put over the first to aid in securing uniform temperature. In this second winding, most of the turns are at the ends of the cylinder as the heat losses tend to be greatest at these points. This winding was also coated with alundum cement. The unit was mounted vertically in a galvanized iron can 45 cm. in diameter and 60 cm. in height using a piece of transite as the covering for the bottom of the cylinder and Sil-O-Cel as the insulating material between the can and the furnace proper. The top of the can is covered with a piece of transite board. The end of the alundum cylinder projects through a hole in the board and is just flush with the top surface. The cover is a piece of transite which also is the bottom of a galvanized iron box filled with Sil-O-Cel. A number of transite disks are fastened to the cover and extend as a plug into the furnace to increase the insulation at the upper end. The temperature is measured by three chromel-alumel thermocouples mounted inside the furnace, one at the middle and the other two near the ends. The cold junctions are immersed in a mixture of ice and water in a Dewar flask. The potentials may be determined with sufficient accuracy by a portable potentiometer. The current in both heating units is controlled by external rheostats. In operation, the maximum observed temperature difference is about 30°, the upper thermocouple reading lower than the other two. However, the upper thermocouple is well above the glass tube which rests in an upright position on the floor of the furnace so that probably the temperature of the tubes and mandrels are maintained uniform within ± 10° which is adequate.

Two carefully lapped mandrels were prepared of tool steel rod by the Department of Metal Processing. The dimensions are respectively 1.496 and 1.801 cm. in diameter and 30.0 and 38.5 cm. in length. Each rod has a projecting portion somewhat smaller in diameter and about 4 cm. long which was needed for holding in grinding the rods before the lapping. The uniformity in diameter was determined on a Zeiss Optimeter to be within ± 0.00025 mm. or 0.002%. The value of 1.496 cm. is less than the 1.72 indicated as the minimum value in the

treatment of the theory of cell design, but the difference will result in increasing the uncertainty in length measurements from 0.001% to only 0.0013% and is therefore not serious.

Pyrex tubing with wall thickness of 2 to 3 mm. was used. The pieces were selected to be as free as possible of flaws and air bubbles. The clean pieces of tubing in appropriate lengths were sealed at one end, the mandrel inserted after the glass had cooled and the other end of the tube fused to an evacuation unit consisting of a mercury vapor diffusion pump backed by a rotary oil vacuum pump. The tube was evacuated to less that 0.1 micron pressure and then sealed off just above the end of the mandrel. The shrinkage of the tubing was accomplished by the following schedule. At 8 A.M. the furnace, which had been cooling overnight and had reached about 250° or 300°, was opened and the tube and rod inserted. The current was turned on and by noon the temperature had reached 650°. The temperature and heating current were carefully correlated so that the temperature did not appreciably exceed 700°. It was maintained there for an hour and then the cooling process was initiated. This was regulated so that by 5 or 6 P.M. the temperature had reached about 500°. The current was then turned off entirely and the tube and rod left in the furnace overnight. The next morning they were removed, the other rod and tube inserted and the process repeated. The cooling from 300° to room temperature took place in the open. The rod and tube had definitely separated by the time they were taken from the furnace. The separation is due, of course, to the fact that the tool steel has a greater coefficient of expansion than the Pyrex glass and therefore in cooling from 700° to room temperature it contracts by a greater amount than the glass. The temperature of separation may be estimated from the measured difference in the diameters of the glass and the rod after treatment. In one case the glass had an inside diameter of 0.713 in. and the steel rod was 0.709 in. in diameter. On the basis of the coefficients of expansion of Pyrex glass and 1.2% carbon steel, the temperature at which the two would have the same diameter would be about 600° so this represents the approximate temperature of separation.

The mandrels were removed by carefully cutting off one of the ends of the tubes on a grinding wheel and carefully slipping out the rods. The clearance between the glass and metal was very slight as evidenced by the piston like action as the rods were withdrawn. The glass showed perfect conformity with the metal even down to the reproduction of the fine lapping scratches. A total of nine tubes were prepared, four of the 18 mm. size and five of the 15 mm. size.

Testing of the Fabricated Glass Tubes.

The direct measurement of the internal diameter of the glass tubes cannot be accomplished with an accuracy of 0.001% with equipment now available. Through the courtesy of the Ford Motor Company, measurements were made on the tubes to ±0.00005 mm. or 0.003% using an Inside Indicator Gage, Size 1, made by the Swedish Gage Company. The gage penetrates to a depth of only about 1 cm. so that two of the tubes were sacrificed by cutting them into a number of short segments. Tests on those segments and on the ends of several of the tubes indicated unpredictable variations in diameter. In some cases the result was as much as 25 microns or 0.2% of the diameter. In other cases the uniformity of diameter was fairly good, being about ± 0.002 mm. or ± 0.015%. The only plausible explanation for such variations seems to be slight differences in wall thickness resulting in continued flow of the glass at some points after others had essentially solidified and separated from the mandrel.

In order to improve the uniformity in bore it was decided to internally lap two of the tubes.

The Internal Lapping of the Tubes.

This work was carried out by the Department of Metal Processing. A series of carefully ground laps were used on the two tubes so treated, one of each diameter being selected. As the glass wore away, it was necessary to prepare a new lap in order to insure proper action of the abrasive. If the fit becomes relatively free, the glass will be ground unevenly. As mentioned earlier, because of this fact it is doubtful if Parker's method produced tubing of a high degree of uniformity. The abrasives were 600 mesh silicon carbide "Crystolon Grain"

used with a light oil and jewelers rouge used with water. The process was continued until testing with a plug gage under water failed to show any variations in diameter. The two tubes are probably uniform in bore within a few ten thousandths of a millimeter although no means is available at present for actually measuring the extent of the variations. The internal surface of the glass is slightly frosty in appearance due to the abrasive action in lapping. No means has been devised as yet whereby the inside of the tubes can be polished without producing irregularities in diameter. The use of a pitch lap would undoubtedly produce an irregular surface.

The tubes have been prepared as nearly perfect as possible so far as their cross sectional areas are concerned. The evaluation of the average cross sectional areas may be accomplished by measurement of the volume by determination of the weight of mercury needed to fill the tube coupled with a direct measurement of the length. Before discussing this point, however, the final step in the preparation of the tubes should be considered, namely, the treatment of the ends.

The Treatment of the Ends of the Tubes.

Introduction.

In order to utilize the tubes as conductivity cells, the ends must be ground plane and at right angles to the tube axes. Furthermore there must be no chipping of the glass at the inside edge as this would alter the uniformity in bore. The necessity for having the ends plane is for convenience in sealing the cell to avoid leaks and also to avoid an increase in the amount of conducting material in the cell as a result of solution lodging between part of the end of the tube and the electrode pressing against it.

It is probably true that a slight departure from perpendicularity of the plane of the end from the axis can be tolerated. The measurement of the tube length gives the average length so that the longer portion of solution on one side of the cell would tend to compensate for the shorter portion on the other. However, as that difference increases, the current distribution in the solution near the electrode is altered and an error would thereby be introduced into the conductivity.

The accuracy of the method of length measurement depends on the perpendicularity being sufficiently exact. The tubes are mounted vertically in this determination. The best measure of attainment of this condition is determined by the horizontality of the plane of the upper end. As was indicated in the discussion of the meter bar, if the length is to be correct within 0.001%, the object must be vertical within 15'. Therefore the planes of the ends of the tubes should be perpendicular to the axes within 15' and preferably less to diminish the uncertainty from this cause. The realization of this condition was made possible by the design, construction and use of special grinding, polishing and testing equipment.

The method of grinding and polishing the ends of the tubes.

To prevent chipping of the internal edge of the glass, a hollow glass plug, ground to a 1 to 25 taper, was cemented into the tube with sealing wax and then ground down until nearly flush with the end of the tube. The end of the tube was then cemented with sealing wax, (heating to 150 to 200° being necessary), into a brass block as shown in Figure 40 and placed on the small leveling table. Three small washers under the block served to raise it and permit the projection of some of the glass to be later ground down. The table had previously been leveled by the use of the machinists level shown at the top of the photograph. This level has a sensitivity of 5.8' per division. In order to align the tube in the brass holder while the wax was still soft, the device shown in place in the upper end of the tube was inserted. A similar piece for the other size tubing is shown dismounted at the right. The sleeve which fits into the tube is slotted so that as the taper plug is drawn upward by tightening the knurled nut which screws on the upper end of the plug, the leaves of the sleeve are expanded against the tube and hold the jig firmly in place. The sleeve was ground to just fit into the tube before being slotted so that the amount of expansion is very slight. The surface on which the level rests is essentially perpendicular to the axis of the sleeve as indicated by a series of readings taken with the device set in a variety of angular positions with respect to the tube. On the assumption that the tube is straight, which is

justifiable when the method of preparation by lapping is considered, the tube axis may be adjusted until it is perpendicular to the plane of the leveling table. This condition is established by moving the tube until the plane upon which the level rests is horizontal. When the sealing wax was fully hardened, the leveling device was removed by releasing the taper plug and pulling the sleeve out of the tube. The end of the tube was then ground down until it was flush with the plane of the brass block. The cast iron lapping block shown at the left in Figure 40 was used for this purpose although it was cut to be circular after the photograph was taken. The grinding abrasives were 400 and 600 mesh silicon carbide with mineral oil as a lubricant and the operation was carried out on a machine built for the purpose. The lapping block was rotated slowly in one direction, the brass block in the opposite direction and at the same time the block was moved back and forth across the lapping surface. This produced the requisite irregularity in motion and served to eliminate much physical labor. When the glass was flush with the brass, the assembly was thoroughly cleaned with gasoline and the lapping block was replaced by a pitch lap. The brass block and glass were then polished on this surface using rouge and water. On only one occasion was a clear glass surface obtained. In the other cases however, there was a definite decrease in the frosty appearance of the ends of the tubes. After polishing, the brass block and tube were thoroughly washed with water, dried and the leveling device inserted. The block was then placed on the previously leveled brass table. Readings on the machinists level served to indicate the departure from perpendicularity of the plane of the end of the tube from the axis, and in no case was it greater than 5'. The tube was separated from the brass block by careful warming and the sealing wax was then removed with alcohol. The other end of the tube was treated in similar fashion except that the leveling device was not used as it tends to chip the edge of the glass on being withdrawn. The level was placed directly on the polished end of the tube. The final tests then indicated the degree of parallelism of the two ends which was within 5' for the two tubes used. The method of operation insures that the variation of either end from being perpendicular to the axis is less than 10' as compared with the 15' which can be tolerated.

The finished tubes are 22.4 and 32.7 cm. in length for the small and large diameters respectively. The resistances when filled with 0.1 D KCl will be between 970 and 990 ohms.

It may be concluded that the tubes have been ground so that the ends are sufficiently smooth, plane and at right angles to the tube axes for their use as conductivity cells to determine the standard value.

The Evaluation of the Cell Constants.

In the method used by others and proposed for this work the cell constant is determined by measurement of the length and volume of the cell. Since, however, this method determines only the average cross sectional area, it involves the assumption that the cross sectional area is uniform throughout. Since the magnitude of the error due to this assumption is uncertain, a direct measurement of the diameters throughout the lengths of the tubes would enhance the accuracy of the work. No equipment is now available which will permit such measurements with the required degree of accuracy. This problem has been submitted to the Engineering Department of the Sheffield Gage Corporation and they have advised that a special attachment can be constructed for their No. 1 Visual Gage which will be sufficiently accurate for the purpose. Readings will be possible with this instrument to about 0.3 micron or to 0.002% of the diameters.

It is obvious that all the measurements required for both methods of cell constant determination and for the final conductivity determinations should be carried out at about the same time so that secular changes in the glass would not serve to diminish the accuracy of the final calculated results. Consequently the actual determinations of the average cross sectional areas, the lengths and the resistances of the cells when filled with 0.1 D KCl have been postponed until the equipment is available for measuring the variations in diameter of the tubes. Preliminary studies serve to indicate, however, that it will be possible to carry out these various measurements in satisfactory manner.

The measurement of the average cross sectional areas.

The determination of the volumes.

The method pointed out above for the determination of the cell constants is based upon independent measurements of the volume and length of each cell. This is in principle the method used by Parker and Parker,[64] but differs in points of technique. They partially filled the tubes under a high vacuum, then released the vacuum and completed the filling by addition of mercury at the top. The excess mercury was carefully removed by pressing a plane piece of glass onto the end of the tube care being taken to avoid entrapping air. The mercury was then poured into a beaker, its temperature taken and the weight found. In the present work the tubes are to be completely filled under a high vacuum, then maintained at a sufficiently constant and measured temperature so that the temperature of the mercury will be known with the necessary accuracy, and finally the mercury will be transferred to a suitable vessel for weighing. The reasons for these modifications will become apparent from the discussion below.

Since the values for the average cross sectional areas are desired with an accuracy as near ±0.001% as possible, the volumes and lengths of the cells should be measured with greater accuracy. The weight of the mercury and its density used in computing the volume must be known therefore, to at least 0.0007%. A mass of this magnitude can be determined on the Troemner No. 00 balance with an accuracy of nearly ± 0.0005% which would be satisfactory. Parker and Parker were interested in determining the volumes to only 0.005% and consequently could employ less accurate methods.

The apparatus for filling the tubes is shown in Figure 41 and in section in Figure 42. The tube is cemented with sealing wax into a ring of steel which is threaded to fit into the steel shell at the bottom. Inside this shell is a plane circular steel plate mounted on a swivel to a screw which carries a fine thread and passes through the bottom of the shell. By turning the screw, the steel plate may be raised until it presses against the end of the tube, effectively closing it. Mercury may be introduced into the shell through the small funnel and removed through the steel stopcock at the bottom. Two small glass windows near the top of the shell permit visual inspection of the interior.

The upper end of the tube is closed by a steel plate with a minute hole in the center which communicates with connections to a vacuum pump. The arrangement as shown in Figure 41 for pressing the upper plate against the tube was found inadequate when mercury was added to the shell. Its weight was sufficient to bend the heavy brass slide and produce a leak at the upper end. The modification shown in Figure 42 was devised to avoid this difficulty. The bakelite ring b is cemented to the tube to hold the brass ring, c, when the three machine screws, m, are tightened. In this way the steel plate is drawn tightly against the end of the tube and held there until the machine screws are released.

The filling of the tube is accomplished by mounting it as described above and closing the lower end with the steel plate inside the shell which is nearly filled with mercury. After sufficient evacuation this bottom plate is lowered slightly and the mercury allowed to enter the tube. When the tube is completely filled, the stopcock at the upper end is closed and the lower plate again pressed tightly against the end. The unit is then removed from the wooden frame of Figure 41 and after removal of the machine screws, the mercury is emptied from the tube by carefully drawing the upper plate away from the end of the tube. The hole in the upper plate is sufficiently small so that none of the mercury is removed from the upper connections.

The density of the mercury must be known to at least 0.0007% in order to realize the desired accuracy in the volume determinations. The temperature coefficient of density of mercury is about 0.18% per degree which requires a control of ±0.04°. To insure uniformity of temperature as well as to obtain accurate knowledge of the average value within these limits, thermostatic control of the filled tube is essential. An air bath maintained at 25.0° would be most convenient for this purpose. Such a device is part of the equipment in the constant temperature room and can very readily be operated at 25.0° with fluctuations of only ±0.03° which is entirely satisfactory.

The stopcock at the top in Figure 41 will necessarily have to be left open until just before the tube is emptied to allow for the expansion or contraction of the mercury.

To avoid the necessity of a temperature correction for the expansion or contraction of the glass, the measurements should be made at 25° within ± 1°.

The weight of mercury will be about 540 g. for the smaller tube and 1175 g. for the larger tube. Both of these quantities may readily be measured with an accuracy of ± 5 mg. on the No. 00 balance described earlier. This uncertainty in weight corresponds to ± 0.001% and ± 0.0005% of the volumes of the respective tubes.

The mercury to be used for these measurements has been carefully purified by the method described on page 28 in connection with the preparation of the thermoregulator for the oil thermostat. It will be necessary to determine its density with an accuracy of ± 0.0007% at a temperature near 25° but known to ± 0.04°. The calculation of the density of the mercury in the tube at the temperature of any individual filling may be found from data in the International Critical Tables.[26]

From this consideration the estimated combined error in the tube volumes due to uncertainties in the weight and density of the mercury is 0.001% to 0.0015%.

The Determination of the Lengths of the Cells.

The method selected for the determination of the cell lengths is based on the scheme which was used by Wolff, Shoemaker and Briggs[94] at the Bureau of Standards for the measurement of the lengths of the tubes used in the determination of the standard ohm. They demonstrated that it was the most accurate method then available for such measurements. Since no better method has been developed, it is selected for this work. The principle is to make the observation on the tubes by some means which simulates as nearly as possible the observations on the meter bar. For this purpose suitably constructed metal blocks with engraved lines placed at the ends of the tubes produce images in the telescopes which have the same appearance as the images of the meter bar. The readings on these lines may be made as accurately as the readings on the meter bar. Two sets of readings are necessary. First the distance between a selected line on each block is found with the tube interposed. Then the tube is removed and the blocks brought together and the distance between the same pair of lines measured again. The difference between these two observations represents the length of the tube.

The blocks used in the measurement of the lengths of the conductivity cells are identical and are made in two parts. To a circular piece of brass 4 mm. thick and 27 mm. in diameter there is screwed a semicircular piece of brass of the same radius and 5 mm. thick. On the diametrical face of this second block there has been soldered a piece of silver 10 mm. long, 5 mm. wide and 1.3 mm. thick. The two faces of the circular block were cut to be as parallel as possible. On the silver surface, three lines were engraved 1.7 mm. in length, 1.0 mm. apart, 15 to 20 microns in width and parallel to the face of the circular block within 3 microns.

The measurements are to be made by sighting on a selected line on each block with the cathetometer and finding the total distance between the two lines by comparison with the meter bar. The tube is to be removed, the blocks placed together and the process repeated. The difference in the two determinations represents the tube length.

A stand has been constructed for holding the tubes and leveling screws are provided for adjusting the tube axis to verticality as indicated by the readings of the machinist's level placed on the upper end of the tube. Attachments have also been provided for holding the blocks against the ends of the tubes and against each other when the tubes are removed. In order to determine the lengths accurately to ± 0.001%, the tubes must be truly vertical within 15' as indicated on page 51 in the discussion of the alignment of the meter bar. The measurements on each tube should be repeated with the tube reversed end for end in order that both end surfaces may be used as aids in establishing verticality. This procedure will verify the degree of parallelism and perpendicularity of the planes of the ends of the tubes as departures from these conditions will be evidenced by apparent differences in tube lengths.

An estimate of the probable accuracy of the length measurements may be made on the basis of the known accuracy of measurements with the meter bar and cathetometer. Eight sightings on lines are necessary for the measurement of the length of a tube. Four of these will be on the lines on the blocks and the remainder will be on the lines of the meter bar. It is assumed in this treatment that all of these readings represent the averages of a number

of pointings of the micrometers. The vertical distance between a line on one of the blocks and the nearest line on the meter bar cannot exceed 0.5 mm. since the meter bar lines are 1.0 mm. apart. The accuracy of measurements of 0.5 mm. may be placed at ±0.0015 mm. on the basis of the accuracy of the tare values of the micrometers. Assuming that in all four instances the vertical distances between the block lines and the meter bar lines are nearly the maximum values, then the total uncertainty in the length of the tube from that source alone may be placed at ±0.003 mm. In addition to this uncertainty the values for the total length are subject to error due to the certification limits of the various intervals of the meter bar. Since there are two such intervals used for each tube measurement and each interval is accurate to ±0.003 mm., the total uncertainty in the tube length may be placed at ±0.005 mm.

As analyzed above, the uncertainty in length measurements corresponds to ±0.0022% for the smaller tube and ±0.0015% for the larger tube.

This analysis does not consider the reproducibility of the measurements on the blocks placed on the tubes. This phase of the problem will only be solved by actual measurements on the tubes made with repeated assemblies and alignments of the tubes.

The uncertainty in the average cross sectional area based upon the probable uncertainties in the length and volume measurements is of the order of ±0.002% to ±0.003%. When these results are combined with the estimated errors in diameters and lengths of the tubes, the probable uncertainty in the cell constants may be estimated at ±0.006% although it may prove to be slightly greater when the actual measurements are carried out.

The Assembly of the Conductivity Cells.

The method of mounting the tubes is shown in Figure 43. Each platinum electrode is carefully lapped to be plane, then cleaned electrolytically with NaOH solution, rinsed thoroughly and plated with platinum black from a solution of H_2PtCl_6 containing a trace of lead acetate. The amount of platinum black needed is determined by experience. Jones and Bollinger[32] have indicated that in the case of solutions of neutral salts, sufficient platinum black may be added to effectively eliminate polarization as demonstrated by the constancy of resistance for various frequencies of the measuring current. Before each assembly of the cell, the electrodes are relapped, cleaned and plated. The cell is filled by mounting it upright on the wooden stand as in Figure 41 and then introducing the solution at the bottom through the hole in the center of the electrode. This hole and the corresponding one for the other electrode are 0.2 mm. in diameter so that the rate of flow of the solution through them is rather slow. When the cell is nearly filled, the upper electrode is raised slightly and the solution allowed to rise until the advancing surface touches it. The electrode is then lowered onto the end of the tube making sure that no air bubbles remain inside the cell. The filled cell can then be flushed out with solution. In the early experiments this procedure invariably resulted in leakage at the glass-to-platinum joints due to the uneven pressure of the electrodes against the tube. This was remedied by the use of brass and bakelite rings described earlier under the determination of the cell volumes. Each electrode then is pulled instead of pressed against the tube; as a result the force is evenly distributed and practically no trouble is experienced with leakage. To protect the glass-platinum junction when the cell is immersed in the oil bath, it is painted over with a rubber preparation known as "Tire Cut Filler." This sets to a rubber like mass around the joint and when painted with shellac prevents liquid from escaping from the cell or oil from creeping in. The glass filling tubes are connected to the electrodes by ground joints, the glass serving as the female parts and the platinum tubes on the back of the electrodes acting as the male parts of the joints. These are lubricated with a stopcock grease made of equal parts of crepe rubber and white vaseline heated at 110° until uniform in body and then repeatedly extracted with boiling water to remove any electrolyte present. This grease is satisfactory in resisting the solvent action of the oil. As shown in Figure 43, electrical contact to the cell is made by steel rods which are threaded to fasten to the electrodes. Each rod is hollow for a portion of its length and contains mercury. A link of heavy copper wire serves to connect each electrode to a test tube filled with mercury and immersed in the oil bath; the mercury in the

test tube is connected in turn to the measuring bridge. A heavy short circuiting link of negligible resistance dipped into these two test tubes effectively removes the cell from the bridge circuit. The resistance of the two smaller links and the steel connectors are too small to be measured on the bridge as proved by attempting to measure the resistance of the cell filled with mercury. No lead correction is therefore necessary in measurements with the cells.

Each electrode is carefully insulated from the rest of the stand by bakelite spacers. Direct tests using the 220 volt direct current and a sensitive microammeter indicated that the resistance between the electrodes and the metal parts of the unit is at least two billion ohms which is ample.

Measurements with both potassium chloride solutions and pure water demonstrated that the method of flushing the cell is inadequate as it fails to remove electrolyte adsorbed on the platinum black of the electrodes. Using the method of filling the cells described above, it is a practical impossibility to avoid this difficulty. A satisfactory remedy found by tests with a modified type of cell built for testing purposes only, is to rinse the cell with a number of portions of solution before filling. This is in accord with the recognized procedure in conductivity measurements. With the cells as described, the flushing process is apparently inefficient. Unfortunately the holes in the electrodes are so small that if the solution is emptied from the assembled cell, an air bubble is entrapped when the cell is refilled which cannot be swept out. This difficulty would be eliminated by a larger hole in one of the electrodes. A larger hole cannot be used because it would produce a more unsymmetrical current distribution. If, however, the enlarged opening were provided with a removable plug which seated flush with the plane of the electrode and could be withdrawn while the cell was being filled or emptied and then replaced, this difficulty would be eliminated. Since it was found that air bubbles would readily pass through a one millimeter opening, this size was selected for the removable plug. The annular space between a snug fitting plug and an opening of that size would be less than the area of the 0.2 mm. opening in the other electrode which in itself is only 0.02% of the total surface of the electrode for the smaller cell and is probably negligible so far as its effect on the cell constant or current distribution is concerned.

Such an electrode has been obtained and will be used in the final measurements.

Resistance measurements on experimental cells filled with solution approximately 0.1 D in KCl indicated that a precision of ±0.001% may readily be realized with the equipment. The allowable time for making a measurement before the conductivity changes appreciably due to the heating effect of the current passing through the cell is at least a minute as compared with the value of thirty seconds used in the analysis of cell design. Although these experiments on the actual measurements of the resistances of the cells when filled with standard value solutions are preliminary in character, they serve to indicate the technique which, if followed, should yield resistance measurements precise to ±0.001% and accurate to ± 0.003% for cells having resistances of about 1000 ohms.

DISCUSSION OF RESULTS

The accuracy of the final conductivity values may be determined from a consideration of the effects of the errors introduced by each measured quantity. In the preceding discussions these various uncertainties have been considered in detail. The actual conductivity values are found from measurements of the resistance and cell constants for the various conductivity cells. In addition to the errors introduced by these measurements, cognizance must be taking of the uncertainty in the temperatures of the solutions considering both the thermostat control and the accuracy of temperature measurement, and in the accuracy and purity of the solutions as prepared. The combined effect of all of these errors may be calculated as

$$\Delta K = \pm\sqrt{(\Delta K)_R^2 + (\Delta K)_{\frac{L}{A}}^2 + (\Delta K)_t^2 + (\Delta K)_s^2} \ .$$

where R, L/A, t and s refer respectively to resistance, cell constant, temperature and solution. By substitution of the various values of these uncertainties as previously calculated, the result

$$\Delta K = \pm\sqrt{(0.003)^2+(0.006)^2+(0.0016)^2+(0.0018)^2}$$

or $\Delta K = \pm 0.0071\%$ is obtained.

As has been previously indicated, the final conductivity values are affected by a systematic error of not more than 0.006% due to the present uncertainty in the knowledge of the value of the sodium sulfate transition temperature on the International Temperature Scale.

The total probable error in this work after the correction for the uncertainty in the value of the sodium sulfate point is eliminated will be $\pm 0.007\%$ which is slightly better than the estimated $\pm 0.009\%$ of the Jones and Bradshaw value for 0.1 D KCl solution.

SUMMARY

(1) A thorough analysis of all previous work bearing on the subject of standard conductivity values has been made.

(2) It was evident from the analysis that discrepancies greatly exceeding the experimental error exist among the present recorded values.

(3) Consideration of recent improvements in the equipment for conductivity measurements and developments in fundamental theory led to a belief that substantial gains in the accuracy of such measurements are attainable.

(4) A careful survey of all the measurements involved and the equipment now available gave reasonable promise that each individual measurement could be made to an accuracy of 0.001%.

(5) A suitable alternating current Wheatstone bridge was designed, built and tested.

(6) Equipment for the control of the temperature of the laboratory to $\pm$ 0.3° was installed.

(7) A potentiometer set up suitable for the calibration of the various resistances was assembled and its resistances calibrated.

(8) The necessary resistances for use with the precision conductivity bridge were calibrated in terms of certified standards.

(9) An oil thermostat which maintains a temperature constant to within 0.001° for indefinite periods was designed and constructed.

(10) A precision resistance bridge to take the place of the Mueller bridge for the determination of temperatures with a resistance thermometer was designed, constructed, tested and calibrated.

(11) The necessary equipment for the precise establishment of the ice point, sodium sulfate point and the steam point was constructed and tested.

(12) For the establishment of the steam point a "Normal" barometer was constructed and tested.

(13) A resistance thermometer was calibrated at the three fixed points by use of the special resistance bridge.

(14) A still for the production of ultrapure conductivity water, together with the necessary accessories for the storage and transfer of the water, was designed and constructed.

(15) A cell for the determination of the conductivity of the water was developed.

(16) The necessary equipment for the rigorous purification of the salt, including devices for fusion and bottling of samples in purified atmospheres was assembled and five samples of KCl were prepared, the original material being obtained from different sources.

(17) A flask was designed, constructed and tested for the preparation of the solutions by weight and for their handling without danger of contamination.

(18) For the selection of proper dimensions for the cells, an analysis from the standpoint of fundamental theory was made.

(19) Methods were worked out and equipment constructed which permitted of the fabrication of glass tubes for the cells having the necessary uniformity of internal diameter and smoothness and parallelism of the end surfaces.

(20) An extremely precise cathetometer was required for measurement of the lengths of the glass tubes. Such an instrument was designed and constructed with the assistance of the Metal Processing Department of the University. It was tested and the periodic and progressive errors of the screws of the filar micrometers were determined.

(21) The necessary apparatus was designed and built for the measurement of the volumes of the cells by means of mercury.

(22) The cell assembly as required for the conductivity measurements involved the construction of special platinum electrodes, end chambers and accessory equipment for filling and mounting the cells.

(23) A large amount of supplementary apparatus was required, all of which had to be assembled and tested and in some cases, calibrated. This included: (1) an auxiliary thermostat for the resistance coils used in the temperature measurements; (2) a vacuum thermocouple; (3) a frequency bridge; (4) a vacuum tube oscillator and an amplifier; (5) a support for the precise alignment of the standard meter bar; (6) the necessary end devices and a support for precision determination of cell lengths; (7) special lighting systems for use with the cathetometer; (8) an automatic ice-shaving machine; (9) an automatic machine for grinding and polishing the ends of the glass cells; (10) a device for calibrating the various levels used; (11) apparatus for the establishment of precise perpendicularity between the ends and axes of the tubes; (12) balances and weights for weighing the salt and solutions.

(24) It was found that a systematic error exists in the sodium sulfate transition temperature which can be evaluated with the requisite accuracy at some future date. When these measurements are made, the conductivity value for 0.1 D KCl obtained using the methods and apparatus developed in this work may be corrected and the value so obtained will possess a probable error of $\pm 0.007\%$ which represents a higher degree of accuracy than has been attained in any previous standard value investigation.

Table 1
Calibration of 1000-ohm Potentiometer Coils

C_1 Designation of Pot. Coil	C_2 Designation of Box Coils	C_2 1st Approx.	ΣC_1 1st Approx.	C_2 2nd Approx.	ΣC_1 2nd Approx.
0-1	900 + 90 + 10 + .5 + .08	1000.79	1000.79	1000.787	1000.79
1-2	900 + 90 + 10 + 1.0 + .01	1001.22	2002.01	1001.218	2002.01
2-3	900 + 90 + 10 + .5 + .09	1000.80	3002.81	1000.796	3002.80
3-4	900 + 90 + 10 + .2 + .09	1000.50	4003.31	1000.497	4003.30
4-5	900 + 90 + 10 + .5 + .01	1000.72	5004.03	1000.719	5004.02
5-6	900 + 90 + 10 + .5 + .05	1000.76	6004.79	1000.757	6004.77
6-7	900 + 90 + 10 + .7 + .05	1000.96	7005.75	1000.968	7005.74
7-8	900 + 90 + 10 + .4 + .08	1000.69	8006.44	1000.687	8006.43
8-9	900 + 90 + 10 + .7 + .02	1000.93	9007.37	1000.930	9007.36
9-10	900 + 90 + 10 + .5 + .03	1000.74	10008.11	1000.737	10008.10
10-11	900 + 90 + 10 + .9 + .09	1001.20	11009.31	1001.196	11009.29
11-12	900 + 90 + 10 + .4 + .06	1000.67	12009.98	1000.668	12009.96
12-13	900 + 90 + 10 + .6 + .09	1000.90	13010.88	1000.896	13010.86
13-14	900 + 90 + 10 + .3 + .05	1000.56	14011.44	1000.558	14011.41
B. of S. 1000	900 + 90 + 9 + .8 + .00	1000.01		1000.01	
Σ999.9	900 + 90 + 10 + .1 + .01	1000.32		1000.298	

Table 2
Calibration of 100-ohm Potentiometer Coils

C_1 Designation of Pot. Coil	C_2 Designation of Box Coils	C_2 1st Approx.	ΣC_1 1st Approx.	C_2 2nd Approx.	ΣC_1 2nd Approx.
0-1	90 + 9 + .9 + .09	100.03	100.03	100.027	100.027
1-2	90 + 10 + .0 + .02	100.06	200.09	100.061	200.088
2-3	90 + 9 + 1.0 + .00	100.04	300.13	100.042	300.130
3-4	90 + 10 + .0 + .02	100.06	400.19	100.061	400.191
4-5	90 + 9 + .9 + .09	100.03	500.22	100.027	500.218
5-6	90 + 9 + 1.0 + .00	100.04	600.26	100.042	600.260
6-7	90 + 9 + 1.0 + .00	100.04	700.30	100.042	700.302
7-8	90 + 10 + .0 + .01	100.05	800.35	100.048	800.350
8-9	90 + 9 + .9 + .09	100.03	900.38	100.027	900.377
B. of S. 100	90 + 9 + .9 + .06	100.00		99.999	
Σ99.9	90 + 9 + .8 + .09	99.93		99.927	

Table 3

Calibration of 10-, 1.0- and 0.1-ohm Potentiometer Coils

Designation of Box Coils	Corr. B	C Designation of Pot. Coils			Corr. B -0.033%B. 1st Approx.	C Calc.	Corr. B- -0.033%B. 2nd Approx.	C Calc.
		x10	x1	x0.1				
100 + 9 + .3 + .04	100.02	1	0	0	99.99	10.00	100.037	10.004
200 + 9 + .3 + .04	200.02	2	0	0	199.95	20.00	200.029	20.003
300 + 9 + .3 + .06	300.04	3	0	0	299.94	29.99	300.028	30.003
400 + 9 + .3 + .07	400.05	4	0	0	399.92	39.99	400.026	40.003
500 + 9 + .3 + .08	500.06	5	0	0	499.89	49.99	500.015	50.002
600 + 9 + .4 + .01	600.09	6	0	0	599.89	59.99	600.025	60.003
700 + 9 + .4 + .03	700.11	7	0	0	699.88	69.99	700.004	70.000
800 + 9 + .4 + .04	800.12	8	0	0	799.86	79.99	800.121	80.012
900 + 9 + .4 + .03	900.11	9	0	0	899.81	89.90	900.005	90.001
10 + 9 + .3 + .01	9.99	0	1	0	10.00	1.00	10.013	1.001
20 + 9 + .3 + .01	19.99	0	2	0	19.99	2.00	20.007	2.001
30 + 9 + .3 + .01	29.99	0	3	0	29.99	3.00	30.004	3.000
40 + 9 + .3 + .01	39.99	0	4	0	39.99	4.00	40.006	4.001
50 + 9 + .3 + .02	50.00	0	5	0	49.99	5.00	50.015	5.002
60 + 9 + .3 + .02	60.00	0	6	0	59.99	6.00	60.007	6.001
70 + 9 + .3 + .02	70.00	0	7	0	69.99	7.00	70.009	7.001
80 + 9 + .3 + .02	80.00	0	8	0	79.98	8.00	80.006	8.001
90 + 9 + .3 + .02	90.00	0	9	0	89.98	9.00	90.000	9.000
9 + .3 + .02	0.00	0	0	0				
1 + .3 + .01	1.00	0	0	1	1.00	.10	1.016	.102
2 + .3 + .01	1.99	0	0	2	1.99	.20	2.011	.201
3 + .3 + .01	3.00	0	0	3	3.00	.30	3.015	.302
4 + .3 + .01	4.00	0	0	4	4.00	.40	4.015	.402
5 + .3 + .01	5.00	0	0	5	5.00	.50	5.015	.502
6 + .3 + .01	6.00	0	0	6	6.00	.60	6.015	.602
7 + .3 + .01	7.00	0	0	7	7.00	.70	7.016	.702
8 + .3 + .00	7.99	0	0	8	7.99	.80	8.011	.801
9 + .3 + .02	9.01	0	0	9	9.01	.90	9.017	.902
0 + .3 + .01	0.00	0	0	0				
900 +90 + 10 + .1 + .01		B. of S. 100			999.99		999.99	

Table 4
Constancy of Resistance of Potentiometer Coils

B Designation	B nominal	C x10	C x1	C x0.1	B Designation	B nominal	C x10	C x1	C x0.1
900+ 90+ 9+ .6+ .02	999.62	0	0	0	900+ 90+ 9+ .5+ .08	999.58	0	5	0
900+ 90+ 9+ .6+ .00	999.60	1	0	0	900+ 90+ 9+ .5+ .08	999.58	0	6	0
900+ 90+ 9+ .6+ .00	999.60	2	0	0	900+ 90+ 9+ .5+ .08	999.58	0	7	0
900+ 90+ 9+ .6+ .00	999.60	3	0	0	900+ 90+ 9+ .5+ .08	999.58	0	8	0
900+ 90+ 9+ .5+ .09	999.59	4	0	0	900+ 90+ 9+ .5+ .08	999.58	0	9	0
900+ 90+ 9+ .5+ .09	999.59	5	0	0	900+ 90+ 9+ .5+ .07	999.57	0	0	1
900+ 90+ 9+ .5+ .09	999.59	6	0	0	900+ 90+ 9+ .5+ .07	999.57	0	0	2
900+ 90+ 9+ .5+ .09	999.59	7	0	0	900+ 90+ 9+ .5+ .07	999.57	0	0	3
900+ 90+ 9+ .5+ .09	999.59	8	0	0	900+ 90+ 9+ .5+ .07	999.57	0	0	4
900+ 90+ 9+ .5+ .07	999.57	9	0	0	900+ 90+ 9+ .5+ .07	999.57	0	0	5
900+ 90+ 9+ .5+ .08	999.58	0	1	0	900+ 90+ 9+ .5+ .07	999.57	0	0	6
900+ 90+ 9+ .5+ .08	999.58	0	2	0	900+ 90+ 9+ .5+ .07	999.57	0	0	7
900+ 90+ 9+ .5+ .08	999.58	0	3	0	900+ 90+ 9+ .5+ .06	999.56	0	0	8
900+ 90+ 9+ .5+ .08	999.58	0	4	0	900+ 90+ 9+ .6+ .02	999.62	0.	0	9

Table 5
Power Consumptions in Resistance Box Calibrations

Decade (ohms)	Current (amps.)	Power (watts/coil)	Fall of Potential (volts)
10000	0.000135	0.00018	1.35
1000	0.00135	0.0018	1.35
100	0.01014	0.0103	1.01
10	0.01014	0.00102	.10
1	0.01008	0.00010	.01
0.1	0.01008	0.00001	.001
0.01	0.01008	0.000001	.0001

Table 6
Measurement of Lead Resistance in Two Dial Box

Designation	R Meas.	R + leads (From Table 8)	Lead Resistance
0.11	0.121	0.134	0.013
0.47	0.480	0.492	0.012
0.79	0.798	0.813	0.015
0.51	0.522	0.534	0.012
0.34	0.352	0.366	0.014
		Avg.	0.013

Table 7
Measurement of Lead Resistance in Five Dial Box

Designation	Location of Potential Leads	R	Lead Resistance
1 x 10	B. Posts	10.011	
1 x 10	Hg Cups	10.000	0.011
1 x 100	B. Posts	100.033	
1 x 100	Hg Cups	100.023	0.010
9 x 10 + 10 x 1	B. Posts	100.017	
9 x 10 + 10 x 1	Hg Cups	100.012	0.005
1 x 1000	B. Posts	1001.219	
1 x 1000	Hg Cups	1001.204	0.015
10 x 1	B. Posts	10.004	
10 x 1	Hg Cups	9.996	0.008
1 x 1	B. Posts	1.011	
1 x 1	Hg Cups	1.001	0.010
9 x 100 + 9 x 10 + 10 x 1	B. Posts	1000.184	
9 x 100 + 9 x 10 + 10 x 1	Hg Cups	1000.173	0.011
		Avg.	0.010

Table 8
Calibration of 1.0-, 0.1- and 0.01-ohm Box Coils
R_1 = 0.99997 ohm

P_1 Nominal	P_1 1st Approx.	P_1 2nd Approx.	P_2 Nominal	P_2 1st Approx.	P_2 2nd Approx.	Desig. of R	R_2 1st Approx.	R_2 2nd Approx.	R Value
.01014	.010143	.010143	.01015	.010153	.010153	0-1	1.001	1.001	1.001
.01014	.010143	.010143	.01015	.010153	.010153	1-2	1.001	1.001	2.002
.01014	.010143	.010143	.01014	.010143	.010143	2-3	1.000	1.000	3.002
.01014	.010143	.010143	.01014	.010143	.010143	3-4	1.000	1.000	4.002
.01013	.010133	.010133	.01014	.010143	.010143	4-5	1.001	1.001	5.003
.01013	.010133	.010133	.01013	.010133	.010133	5-6	1.000	1.001	6.003
.01013	.010133	.010133	.01014	.010143	.010143	6-7	1.001	1.001	7.004
.01013	.010133	.010133	.01014	.010143	.010143	7-8	1.001	1.001	8.005
.01013	.010133	.010133	.01002	.010023	.010023	8-9	.989	.989	8.994
.01013	.010133	.010133	.01014	.010143	.010143	9-10	1.001	1.001	9.995
.01013	.010133	.010133	.00116	.001160	.001161	.1	.114	.115	
.01013	.010133	.010133	.00218	.002180	.002181	.2	.215	.215	
.01013	.010133	.010133	.00319	.003189	.003191	.3	.315	.315	
.01013	.010133	.010133	.00420	.004199	.004200	.4	.414	.414	
.01013	.010133	.010133	.00521	.005209	.005211	.5	.514	.514	
.01013	.010133	.010133	.00622	.006219	.006221	.6	.614	.614	
.01012	.010123	.010123	.00723	.007229	.007230	.7	.714	.714	
.01012	.010123	.010123	.00824	.008239	.008242	.8	.814	.814	
.01012	.010123	.010123	.00925	.009248	.009250	.9	.914	.914	
.01012	.010123	.010123	.01027	.010273	.010273	1.0	1.015	1.015	
.01012	.010123	.010123	.00020	.000200	.000200	.01	.020	.020	
.01013	.010133	.010133	.00033	.000330	.000330	.03	.033	.033	
.01013	.010133	.010133	.00040	.000400	.000400	.03	.040	.040	
.01012	.010123	.010123	.00052	.000520	.000520	.04	.051	.051	
.01012	.010123	.010123	.00061	.000610	.000610	.05	.060	.060	
.01012	.010123	.010123	.00072	.000720	.000720	.06	.071	.071	
.01012	.010123	.010123	.00079	.000790	.000790	.07	.078	.078	
.01012	.010123	.010123	.00091	.000910	.000910	.08	.090	.090	
.01012	.010123	.010123	.00100	.001000	.001000	.09	.099	.099	
.01012	.010123	.010123	.00111	.001110	.001110	.10	.110	.110	

Table 9

Calibration of 10-ohm Box Coils

R_1 = 10.0002 ohms

Designation	P_1 Reading	P_1 Corr. by 2nd Approx.	P_2 Reading	P_2 Corr. by 2nd Approx.	R_2 Calc.	ΣR_2
0-1	.10175	.10183	.10175	.10183	10.000	10.000
1-2	.10174	.10182	.10172	.10180	9.998	19.998
2-3	.10173	.10181	.10174	.10182	10.000	29.998
3-4	.10173	.10181	.10178	.10186	10.005	40.003
4-5	.10173	.10181	.10173	.10181	10.000	50.003
5-6	.10173	.10181	.10174	.10182	10.000	60.003
6-7	.10173	.10181	.10172	.10180	9.999	70.002
7-8	.10173	.10181	.10179	.10187	10.006	80.008
8-9	.10173	.10181	.10176	.10184	10.003	90.011
Σ1 ohm coils	.10173	.10181	.10169	.10177	9.996	
1x10 at B. Posts	.10173	.10181	.10184	.10192	10.011	
10x1 at B. Posts	.10174	.10182	.10178	.10186	10.004	

Table 10

Calibration of the 100-ohm Box Coils

R_1 = 99.999 ohms

Designation	P_1 Reading	P_1 Corr. by 2nd Approx.	P_2 Reading	P_2 Corr. by 2nd Approx.	R_2 Calc.	ΣR_2
0-1	1.02125	1.02207	1.02150	1.02232	100.023	100.023
1-2	1.02124	1.02206	1.02151	1.02233	100.025	200.048
2-3	1.02123	1.02205	1.02136	1.02218	100.012	300.060
3-4	1.02123	1.02205	1.02149	1.02231	100.024	400.084
4-5	1.02122	1.02204	1.02133	1.02215	100.010	500.094
5-6	1.02122	1.02204	1.02137	1.02219	100.014	600.108
6-7	1.02121	1.02203	1.02124	1.02206	100.002	700.110
7-8	1.02120	1.02202	1.02151	1.02233	100.029	800.139
8-9	1.02119	1.02201	1.02149	1.02231	100.028	900.167
9x10+10x1	1.02116	1.02198	1.02129	1.02211	100.012	
9x10+10x1 at Binding Posts	1.02030	1.02112	1.02048	1.02130	100.017	
100 at B. Posts	1.02028	1.02110	1.02063	1.02145	100.033	

Table 11

Calibration of 1000-ohm Box Coils

R_1 = 1000.01 ohms

Designation	P_1 Reading	P_1 Corr. by 2nd Approx.	P_2 Reading	P_2 Corr. by 2nd Approx.	P_2 Calc.	ΣR_2
0-1	1.37164	1.372757	1.37328	1.374897	1001.204	1001.204
1-2	1.37145	1.372567	1.37250	1.373617	1000.774	2001.978
2-3	1.37141	1.372527	1.37312	1.374237	1001.255	3003.233
3-4	1.37136	1.372477	1.37281	1.373927	1001.066	4004.299
4-5	1.37131	1.372427	1.37322	1.374337	1001.401	5005.699
5-6	1.37127	1.372387	1.37278	1.373897	1001.110	6006.809
6-7	1.37123	1.372347	1.37242	1.373537	1000.877	7007.686
7-8	1.37120	1.372317	1.37362	1.374737	1001.773	8009.459
8-9	1.37114	1.372257	1.37263	1.373747	1001.095	9010.554
Σ1000 at B. Posts	1.37193	1.373047	1.37217	1.373287	1000.184	
1000 at B. Posts	1.37176	1.372877	1.37342	1.374537	1001.219	

Table 12

Calibration of 10000-ohm Box Coils

R_1 = 9999.4 ohms

Designation	P_1 Reading	P_1 Corr. by 2nd Approx.	P_2 Reading	P_2 Corr. by 2nd Approx.	R_2 Calc.	ΣR_2
0-1	1.37698	1.378097	1.38732	1.388441	10074.46	10074.46
1-2	1.37698	1.378097	1.39150	1.392625	10104.81	20179.27
2-3	1.37698	1.378097	1.38561	1.386732	10062.05	30241.32
3-4	1.37697	1.378087	1.38325	1.384372	10045.00	40286.32
4-5	1.37695	1.378067	1.38599	1.387112	10065.08	50351.40
5-6	1.37694	1.378057	1.38662	1.387742	10069.68	60421.08
6-7	1.37692	1.378037	1.38408	1.385202	10051.39	70472.47
7-8	1.37691	1.378027	1.39147	1.392595	10105.10	80572.57
8-9	1.37690	1.378017	1.38568	1.386802	10063.15	90640.72
10000 at B. Posts	1.38163	1.387752	1.39201	1.393134	10074.48	
Σ10000 at B. Posts	1.38045	1.381572	1.38198	1.383102	10010.47	
Σ10000	1.38060	1.381721	1.38214	1.383262	10010.55	

Table 13

Comparison of 10 x 1000-ohm Potentiometer Coils with 10000-ohm Standard

B Nominal	C_1 Designation	C_2 5 + 2 Dial Box Desig.	C_2 Nominal	C_2 2nd Approx.	C_2 2nd Approx.
10018.7	10 x 1000	9000+900+90+7+.4+.00	9997.40	10008.11	10008.110
10010.0	10000 Std.	9000+900+80+8+.7+.00	9988.70	9999.4	9999.4

Table 14

Calibration of Vacuum Thermocouple

Ammeter Reading in milliamperes	Voltmeter Reading in millivolts
(full scale = 5.0 ma.)	(full scale = 1.0 mv.)
0.100	0.021
0.150	0.048
0.200	0.150
0.300	0.215
0.350	0.294
0.400	0.384
0.450	0.482
0.500	0.618
(full scale = 50.0 ma.)	
0.55	0.652
0.60	0.759
0.65	0.893
	(full scale = 10.0 mv.)
0.65	3.12
0.70	3.63
0.80	4.56
0.90	5.55
1.00	6.64
1.10	7.73
1.20	8.84
1.30	9.86

Table 15
Values of Resistance Thermometer Coils

Designation	Value Originally Specified	L & N Value Feb. 1934	Calibration May 1934	Calibration Jan. 1935
T_1	26.593	26.5933	26.59312	26.59325
T_2	29.175	29.1755	29.17551	29.17551
T_3	29.933	29.9332	29.93266	29.93271
T_4	36.763	36.7647	36.76426	36.76441
L	28.722	28.7231	28.72306	28.72304
R_1	26.381	26.3817	26.38157	26.38168
R_2	28.940	28.9406	28.94025	28.94030
R_3	29.690	29.6912	29.69095	29.69105
R_4	36.452	36.4531	36.45236	36.45250

Table 16
Calibration of Slide Wire

R_1 in (R_3) Reading	Resistance
399.87	26.34656
410.00	26.35012
420.06	26.35367
429.95	26.35711
440.11	26.36069
449.98	26.36415
540.10	26.39576
549.98	26.39923
560.03	26.40273
570.05	26.40626
580.09	26.40975
589.92	26.41321

R_2 in (R_3) Reading	Resistance
300.00	28.86352
310.04	28.86736
320.05	28.87121
330.21	28.87508
340.03	28.87885
350.06	28.88273
359.93	28.88651
369.78	28.89029
379.89	28.89415
390.28	28.89810
400.02	28.90185
409.94	28.90567
420.04	28.90955
430.04	28.91340
439.98	28.91722
449.80	28.92100
460.00	28.92490
470.02	28.92875
479.93	28.93255
490.02	28.93644
499.94	28.94028
510.05	28.94418
520.00	28.94801
529.91	28.95184
539.97	28.95571
549.94	28.95956
559.92	28.96338

R_3 in (R_3) Reading	Resistance
200.70	29.57318
210.16	29.57689
220.04	29.58080
230.52	29.58490
240.86	29.58904
250.58	29.59282
260.34	29.59664
269.86	29.60038
280.09	29.60440
290.06	29.60832
300.00	29.61227
310.06	29.61623
319.90	29.62010
329.84	29.62398
339.96	29.62797
350.02	29.63196
360.16	29.63594
370.23	29.63993
379.89	29.64371
390.06	29.64766
400.00	29.65160
409.97	29.65551
420.22	29.65957
429.97	29.66343
439.93	29.66734
450.13	29.67136
460.06	29.67527
470.02	29.67920
480.10	29.68316
489.90	29.68706
499.94	29.69103
510.04	29.69501
520.02	29.69898
530.00	29.70294
540.04	29.70688
550.06	29.71084
559.97	29.71473
570.14	29.71874
580.06	29.72265
589.92	29.72652
599.96	29.73052
609.94	29.73442
620.07	29.73841
629.94	29.74234
640.00	29.74634
650.02	29.75028
660.06	29.75421
670.04	29.75818
679.92	29.76207
689.96	29.76604
700.24	29.77013
710.10	29.77401
719.93	29.77791
730.02	29.78189
740.06	29.78587
750.10	29.78985
760.32	29.79386
769.90	29.79769
779.98	29.80166
790.06	29.80567
800.14	29.80968

R_4 in (R_3) Reading	Resistance
0.22	36.21111
10.01	36.21583
20.02	36.22069
29.80	36.22545
40.00	36.23036
50.00	36.23516
59.86	36.23989
69.81	36.24473
80.11	36.24968
90.23	36.25453
100.13	36.25930
109.92	36.26397
119.81	36.26875
130.17	36.27378
140.02	36.27854
150.02	36.28339
159.89	36.28813
169.85	36.29295
180.04	36.29784
189.98	36.30262
199.97	36.30746
210.12	36.31235
219.96	36.31714
230.08	36.32199
239.83	36.32672
250.01	36.33162
260.00	36.33642
269.96	36.34124
280.04	26.34609
290.07	36.35095
300.08	36.35583
310.26	36.36071
320.06	36.36548
330.03	36.37025
339.92	36.37502
349.86	36.37989
359.96	36.38475
369.94	36.38960
379.97	36.39442
389.96	36.39922
399.99	36.40409
410.21	36.40901
420.08	36.41381
429.79	36.41848
439.97	36.42345
449.98	36.42829
460.06	36.43314
469.92	36.43794
479.94	36.44276
490.01	36.44766
499.97	36.45248
510.01	36.45737
520.21	36.46232
530.06	36.46710
539.88	36.47186
549.89	36.47672
560.01	36.48160
569.92	36.48643
580.07	36.49131
590.08	36.49614
600.03	36.50096
609.93	36.50575
620.06	36.51066
630.01	36.51552
640.19	36.52046
650.01	36.52521
659.98	36.53002
670.03	36.53492
679.98	36.53973
689.92	36.54455
699.97	36.54945
709.97	36.55429
720.00	36.55917
730.03	36.56404
740.04	36.56891
750.17	36.57384
759.95	36.57856
769.98	36.58348
780.17	36.58843
790.11	36.59327
799.98	36.59804
810.10	36.60295
820.16	36.60782
830.23	36.61274
840.03	36.61753
849.91	36.62232
860.03	36.62715
870.01	36.63206
880.25	36.63705
890.01	36.64179
900.10	36.64671
910.26	36.65162
920.05	36.65641
930.01	36.66127
940.06	36.66615
950.04	36.67105
960.27	36.67594
970.02	36.68072
980.07	36.68560
990.20	36.69052
999.45	36.69500

Table 17
Thermometer Calibration at the Ice Point

Run No. 3

Condition	Resistance	Deviation
As filled	25.50535	-.00037
1st washing	25.50564	
Drained	25.50564	
2nd washing	25.50565	
3rd washing	*25.50569	-.00003
Drained	25.50574	+.00002
4th Washing (10 hours later)	25.50572	.00000
Drained	25.50573	+.00001
5th washing	25.50570	-.00002
Drained	25.50571	-.00001
Average up to	*25.50572	Average ±.000015

Run No. 4

As filled	*25.50552	-.00019
1st washing	25.50572	+.00001
Drained	25.50571	.00000
2nd washing	25.50573	+.00002
Drained	25.50578	+.00007
3rd washing	25.50574	+.00003
Drained	25.50570	-.00001
4th washing	25.50565	-.00006
Drained	25.50567	-.00004
Average up to*	25.50571	Average ±.00003

Run No. 5

As filled	25.50561	-.00006
1st washing	25.50576	
Drained	*25.50567	.00000
2nd washing	25.50567	.00000
Drained	25.50566	-.00001
3rd washing	25.50570	+.00003
Drained	25.50564	-.00003
4th washing	25.50566	-.00001
Drained	25.50568	+.00001
Average up to*	25.50567	Average ±.00001

Run No. 6

As filled	25.50544	-.00030
1st washing	25.50568	
Drained	25.50566	
2nd washing	*25.50572	-.00002
3rd washing	25.50576	+.00002
Drained	25.50570	-.00004
4th washing	25.50575	+.00001
Five hours later	25.50575	+.00001
Drained	25.50569	-.00005
5th washing (10 hours later)	25.50579	+.00005
Drained	25.50578	+.00004
Average up to*	25.50574	Average ±.00003

Table 18
Thermometer Calibration at the Sodium Sulfate Point

Sample	Time	H_2O Temp.	Resistance	Average of Values marked with *	Deviations
A	11:15 AM	32.26	28.76974		
	11:31	32.27	28.76963*		+.00001
	11:47	32.28	28.76967*		+.00003
	12:07 PM	32.30	28.76965*	28.76964	+.00001
	1:13	32.30	28.76961*		-.00003
	1:55	32.30	28.76963*		-.00001
	3:37	32.50	28.76954		
	3:52	32.50	28.76955		Avg. ±.00002
	4:22	32.51	28.76956		
	4:40	32.51	28.76949		
	4:52	32.51	28.76947		
	9:12	32.55	28.76954		
	9:40	32.55	28.76950		
	11:50	31.40	28.76951		
	12:10 AM	31.40	28.76956		
B	10:55 AM	32.50	28.76961		
	11:13	32.50	28.76966*		+.00004
	11:47	32.50	28.76965*		+.00003
	12:17 PM	32.50	28.76963*		+.00001
	12:33	32.50	28.76970*		+.00008
	2:11	32.28	28.76963*		+.00001
	2:43	32.25	28.76965*		+.00003
	3:11	32.25	28.76958*	28.76962	-.00004
	3:37	32.25	28.76959*		-.00003
	4:16	32.26	28.76961*		-.00001
	9:00	33.72	28.76964*		+.00002
	9:30	33.72	28.76956*		-.00006
	10:28	31.13	28.76955*		-.00007
	11:00	31.14	28.76957*		-.00005
					Avg. ±.00004
C	1:34 PM	32.50	28.76979		
	2:16	32.50	28.76977		
	2:35	32.50	28.76977		
	3:14	32.50	28.76969*		+.00008
	3:35	32.50	28.76967*		+.00006
	4:11	32.50	28.76963*		+.00002
	4:25	32.50	28.76964*		+.00003
	7:03	32.27	28.76959*		-.00002
	8:03	32.27	28.76957*		-.00004
	8:49	34.00	28.76964*	28.76961	+.00003
	9:25	34.00	28.76966*		+.00005
	9:40	34.00	28.76958*		-.00003
	10:55	31.10	28.76961*		.00000
	11:23	31.13	28.76958*		-.00003
	12:27 AM	32.60	28.76955*		-.00006
	12:42	32.60	28.76953*		-.00007
					Avg. ±.00004

Table 19
Correction Table for Lower Micrometer Telescope

	0	1	2	3	4	5	6	7	8	9
20	+.037	+.036	+.033	+.020	+.013	+.014	+.016	+.011	+.077	+.016
21	+.031	+.029	+.026	+.013	+.006	+.007	+.009	+.004	.000	+.008
22	+.026	+.024	+.020	+.007	.000	.000	+.005	-.003	-.007	+.001
23	+.021	+.018	+.015	+.001	-.006	-.006	-.003	-.010	-.014	-.005
24	+.016	+.013	+.009	-.004	-.013	-.012	-.010	-.016	-.020	-.012
25	+.012	+.008	+.004	-.009	-.018	-.018	-.016	-.022	-.026	-.017
26	+.008	+.005	.000	-.014	-.023	-.023	-.021	-.026	-.031	-.023
27	+.004	+.001	-.004	-.018	-.027	-.027	-.026	-.031	-.035	-.027
28	+.002	-.001	-.006	-.020	-.030	-.030	-.029	-.034	-.038	-.030
29	+.001	-.002	-.007	-.022	-.032	-.033	-.031	-.036	-.039	-.031
30	.000	-.003	-.007	-.023	-.033	-.034	-.033	-.037	-.039	-.032
31	+.001	-.002	-.005	-.021	-.032	-.033	-.032	-.036	-.037	-.031
32	+.003	.000	-.003	-.018	-.029	-.030	-.030	-.033	-.035	-.028
33	+.005	+.002	.000	-.014	-.026	-.027	-.027	-.030	-.032	-.023
34	+.007	+.005	+.002	-.011	-.024	-.025	-.025	-.027	-.029	-.019
35	+.009	+.007	+.005	-.009	-.022	-.023	-.022	-.024	-.026	-.017
36	+.012	+.010	+.007	-.007	-.020	-.020	-.019	-.021	-.023	-.014
37	+.015	+.013	+.010	-.005	-.018	-.018	-.016	-.017	-.020	-.012
38	+.019	+.017	+.013	-.003	-.015	-.015	-.013	-.013	-.015	-.009
39	+.023	+.021	+.017	+.001	-.012	-.012	-.009	-.009	-.011	-.006
40	+.028									

Table 20
Accuracy in Length Measurements with Cathetometer

Interval Measured	Bureau of Standards certified values in mm.	As measured with Lower Telescope in mm.			As measured with Upper Telescope in mm.		
0.0 to -0.1	0.102	0.100	0.100	0.099	0.102	0.102	0.101
-0.1 to -0.2	0.099	0.101	0.102	0.101	0.099	0.101	0.101
-0.2 to -0.3	0.100	0.100	0.098	0.099	0.099	0.099	0.100
-0.3 to -0.4	0.100	0.099	0.101	0.098	0.099	0.102	0.099
-0.4 to -0.5	0.101	0.102	0.101	0.102	0.101	0.099	0.101
-0.5 to -0.6	0.100	0.099	0.099	0.100	0.098	0.098	0.101
-0.6 to -0.7	0.099	0.100	0.100	0.100	0.101	0.102	0.102
-0.7 to -0.8	0.100	0.101	0.100	0.100	0.102	0.101	0.097
-0.8 to -0.9	0.099	0.100	0.100	0.099	0.099	0.099	0.101
-0.9 to -1.0	0.097	0.095	0.097	0.098	0.095	0.096	0.096
0.0 to 1.0	1.000		1.001			1.001	
1.0 to 2.0	1.000		0.999			0.998	
2.0 to 3.0	0.999		1.000			0.999	

Table 21
Thermometer Calibration at the Steam Point

	Time	Pressure mm. of Hg	Resist.	Interpol. Pressure	Calc. Temp.	Calc.δ	R_{100}	Δ
May 5, 1936	8:45 AM		35.41999	742.08	99.3349	1.469	35.48540	+.00021
	8:55	742.07						
	9:02		35.42000	742.06	99.3342	1.468	35.48548	+.00029
	9:10	742.04						
	9:19		35.41951	742.00	99.3319	1.472	35.48521	+.00002
	9:30	741.94						
May 20, 1936	11:25 AM	747.36						
	11:37		35.43955	747.48	99.5369	1.474	35.48509	-.00010
	11:44	747.52						
	11:55		35.43949	747.54	99.5391	1.478	35.48481	-.00038
	12:01 PM	747.52						
	1:51	747.28						
	2:10		35.43914	747.34	99.5317	1.472	35.48519	.00000
	2:16	747.35						
	2:25		35.32937	747.34	99.5317	1.469	35.48543	+.00024
	2:35	747.32						
June 3, 1936	2:25 PM	738.41						
	2:40		35.40584	738.36	99.1950	1.475	35.48500	-.00019
	2:48	738.36						
	2:58		35.40599	738.39	99.1961	1.474	35.48504	-.00015
	3:05	738.42						
	3:11		35.40619	738.44	99.1980	1.474	35.48506	-.00013
	3:23	738.44						
	3:32		35.40620	738.42	99.1973	1.473	35.48511	-.00008
	3:46	738.35						
	3:57		35.40596	738.27	99.1917	1.468	35.48545	+.00026
	4:04	738.25						
	4:13		35.40567	738.26	99.1913	1.472	35.48520	+.00001
	4:21	738.31						
						Avg. 1.472	35.48519	±.00016

Table 22
Values Used in Calculation of Error in Temperature Measurement at 25°

$R_0 = 25.5$	$\Delta R_0 = 0.00004$	$(\Delta t)_{R_0} = 0.00007$
$R_N = 28.8$	$\Delta R_N = 0.00003$	$(\Delta t)_{R_N} = 0.00026$
$R_S = 35.4$	$\Delta R_S = 0.00003$	$(\Delta t)_{R_S} = 0.00000$
$t_N = 32.4$	$\Delta t_N = 0.0005$	$(\Delta t)_{t_N} = 0.00043$
$t_S = 99.5$	$\Delta t_S = 0.0005$	$(\Delta t)_{t_S} = 0.00001$
	$\Delta R_t = 0.00003$	$(\Delta t)_{R_t} = 0.00030$

TABLE OF FIGURES AND DRAWINGS

Figure No.

1 Simple Wheatstone Bridge Circuit.
2 Conductivity Bridge Circuit.
3 Conductivity Bridge and Thermostat.
4 Oscillator Circuit.
5 Amplifier Circuit.
6 Frequency Bridge Circuit.
7 Electrical Characteristics of Measuring Arm of Conductivity Bridge.
8 Vectorial Relations of Currents in Measuring Arm of Conductivity Bridge.
9 Impedance and Admittance Triangles for Measuring Arms of Conductivity Bridge.
10 Room Temperature Regulator.
11 Electrical Circuit of Wolff Potentiometer.
12 Hook-up for Potentiometer Calibration.
13 Connections for Thermostat Regulator.
14 Heater Control Circuit for Thermostat.
15 Lead Arrangements for Resistance Thermometers.
16 Thermometer Bridge Circuit.
17 Thermometer Bridge and Potentiometer Assembly.
18 Vacuum Tube Circuit for Thermometer Bridge Thermostat.
19 Thyratron Tube Circuit for Thermometer Bridge Thermostat.
20 Combinations for Thermometer Bridge Coil Calibration.
21 Stand for Thermometer Bridge Coil Calibration.
22 Ice Point Apparatus.
23 Ice Point Assembly.
24 Ice Shaving Machine
25 Thermometer and Sodium Sulfate Point Apparatus.
26 Glass Vessel for Sodium Sulfate Point.
27 Hypsometer.
28 Cathetometer and Barometer Assembly.
29 Upper Limb of Barometer.
30 Lower Limb of Barometer.
31 Diagram of Barometer Glasswork.
32 Lower Cathetometer Telescope and Shaft Mounting.
33 Meter Bar and Support.
34 Diagram for Analysis of Meter Bar Deformation.
35 Time-Pressure Curves for Steam Point Calibration.
36 Flask for Preparation of Solutions.
37 Conductivity Water Still.
38 Conductivity Water Cell.
39 Apparatus for Fusion of KCl.
40 Equipment for Grinding and Testing Ends of Cells.
41 Assembly of Mercury Filling Apparatus.
42 Section Drawing of Mercury Filling Apparatus.
43 Assembled Conductivity Cell.

* * * * *

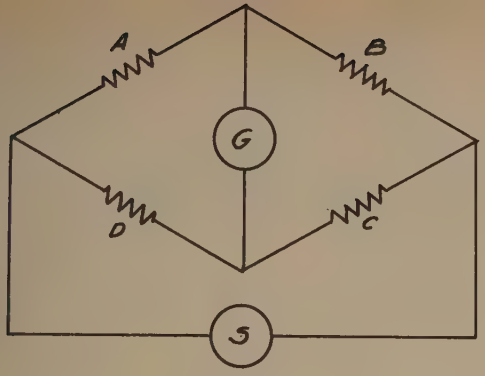


Fig. 1

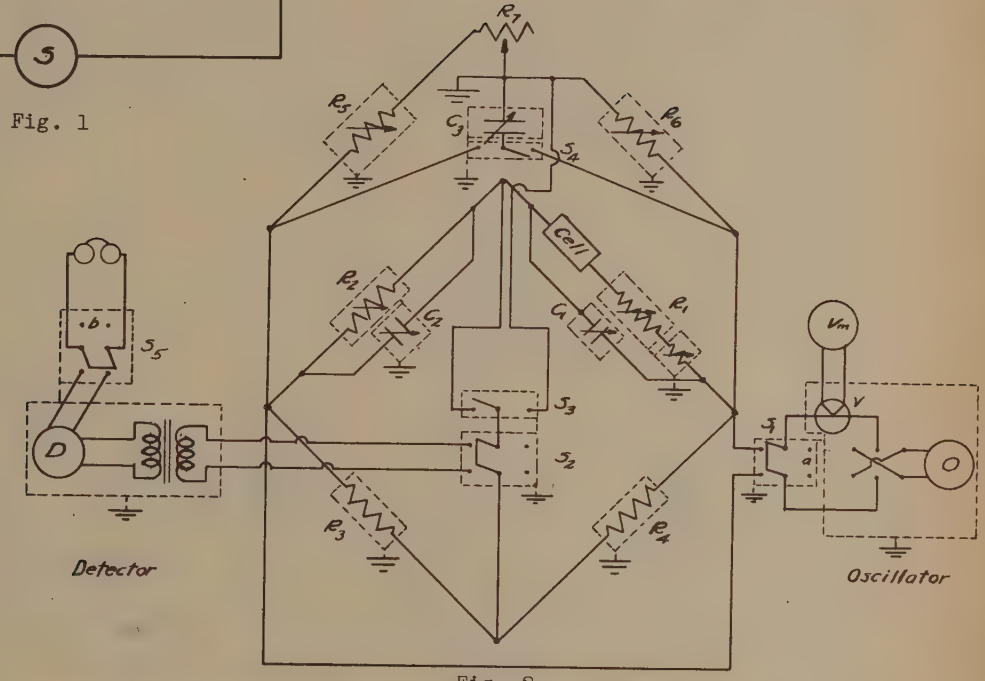


Fig. 2

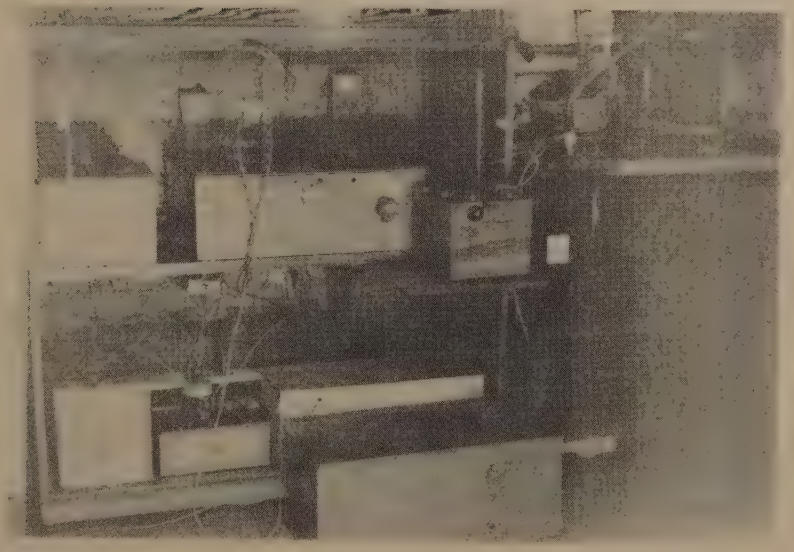


Fig. 3

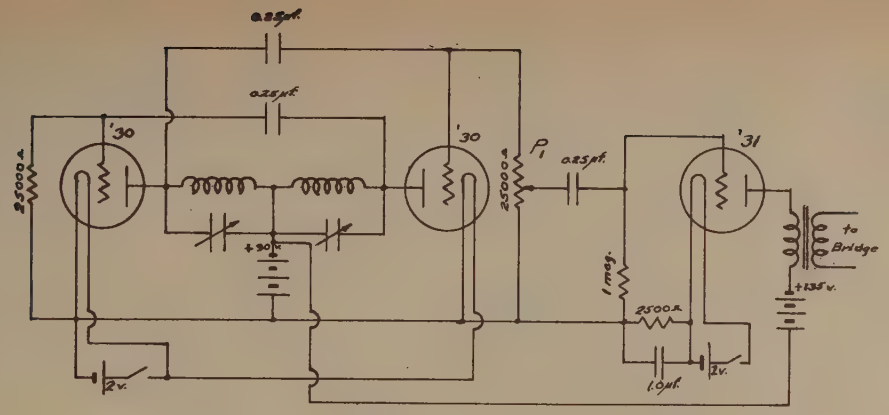


Fig. 4

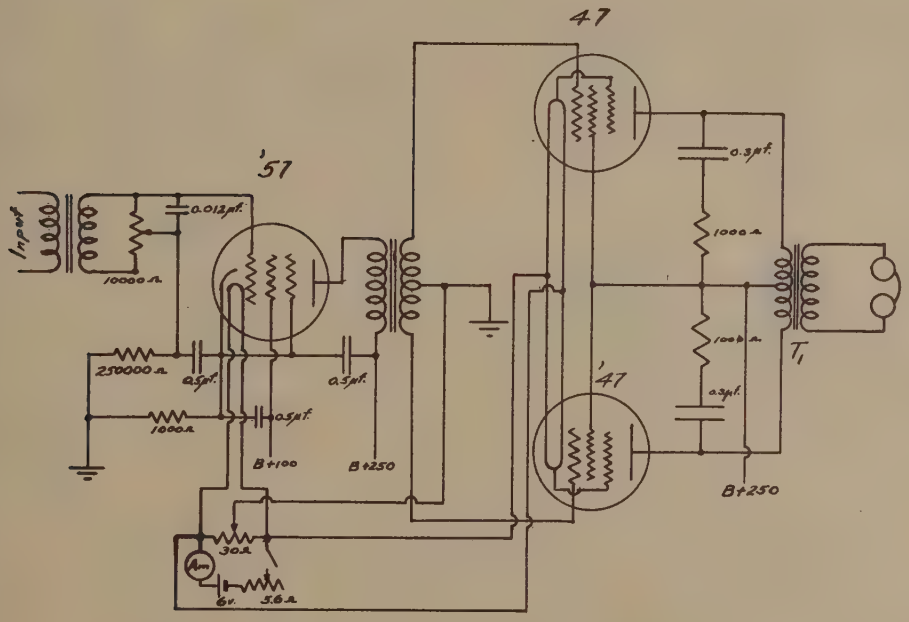


Fig. 5

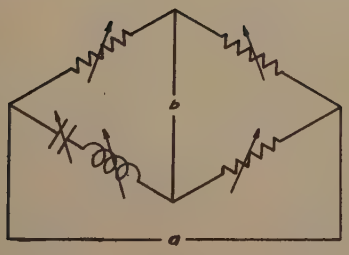


Fig. 6

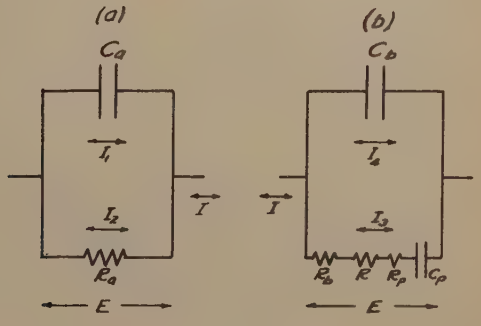


Fig. 7

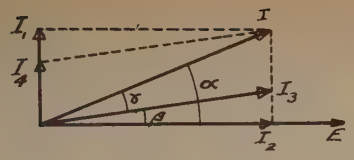


Fig. 8

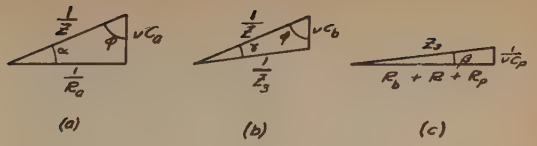


Fig. 9

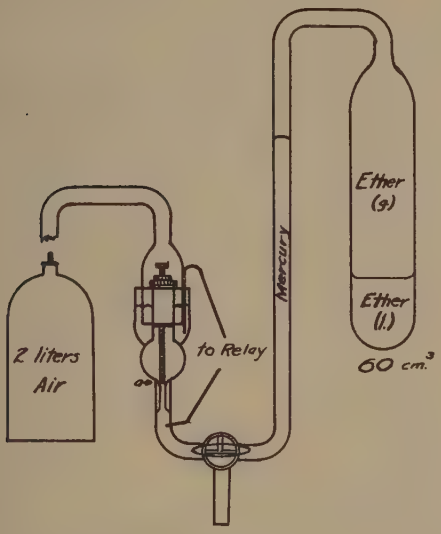


Fig. 10

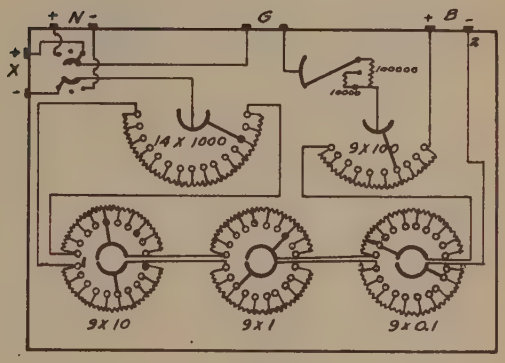


Fig. 11

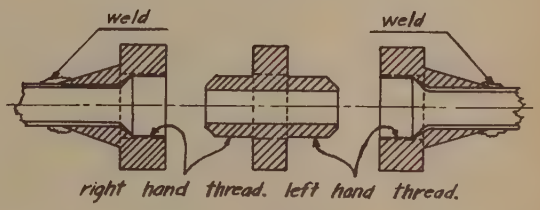


Fig. 13

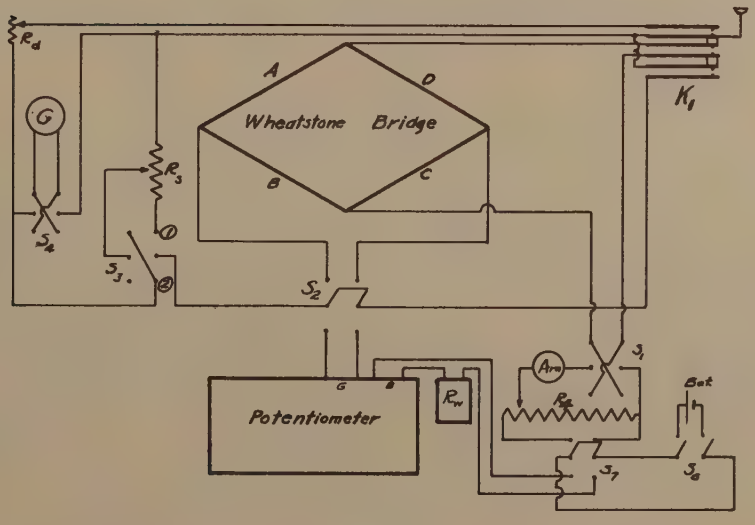


Fig. 12

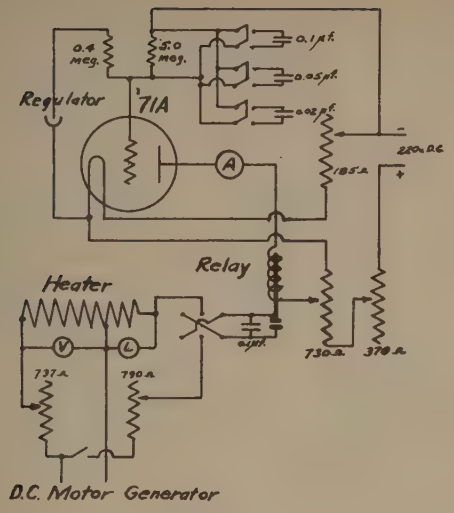


Fig. 14

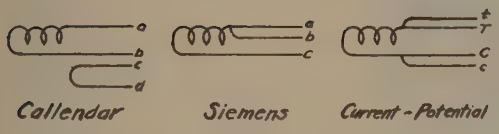


Fig. 15

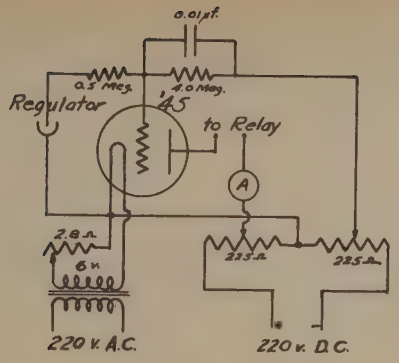


Fig. 18

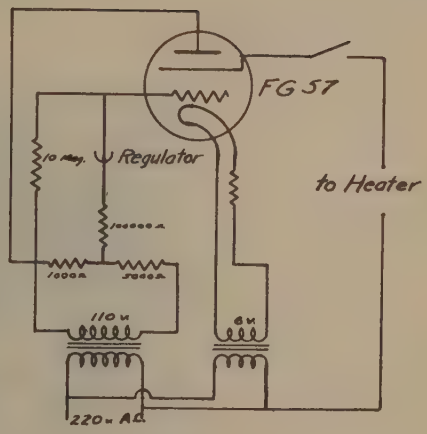


Fig. 19

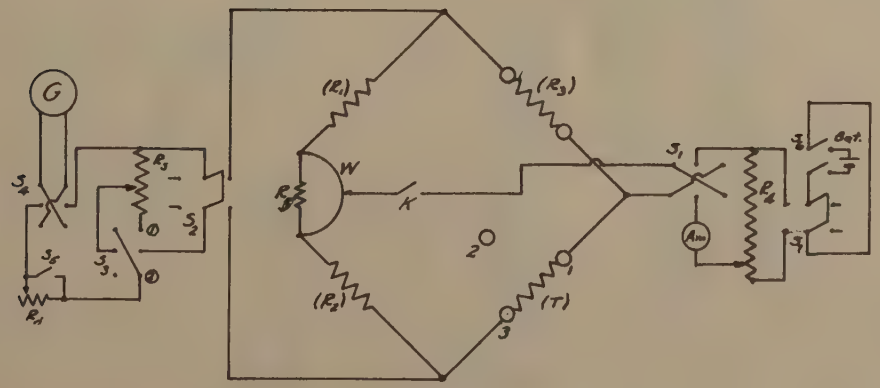


Fig. 16

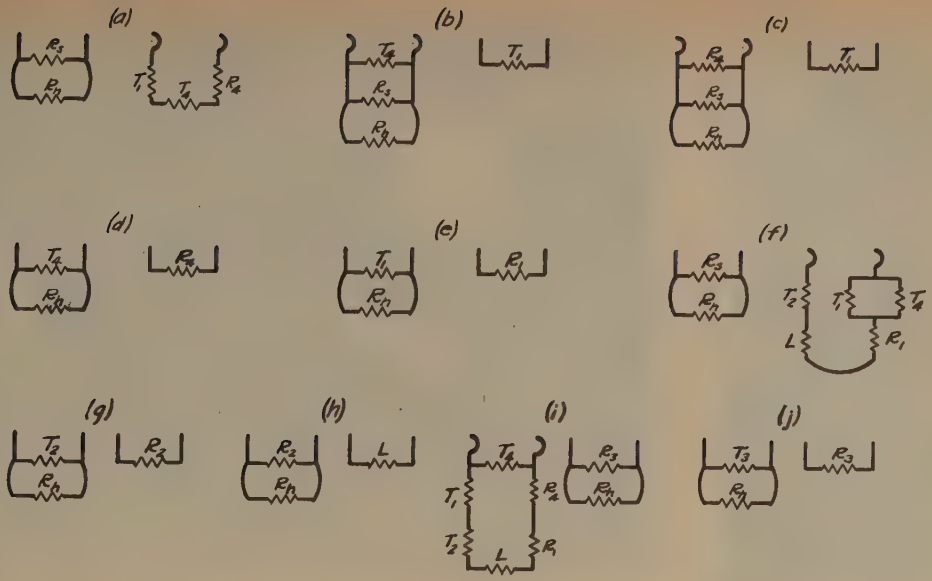


Fig. 20

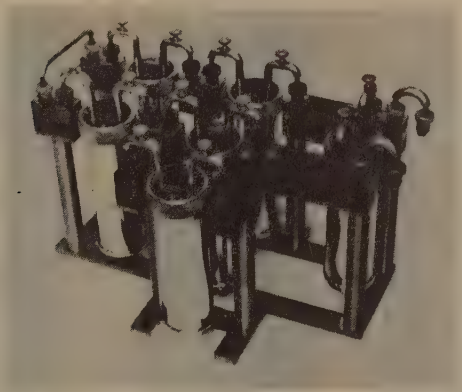


Fig. 21

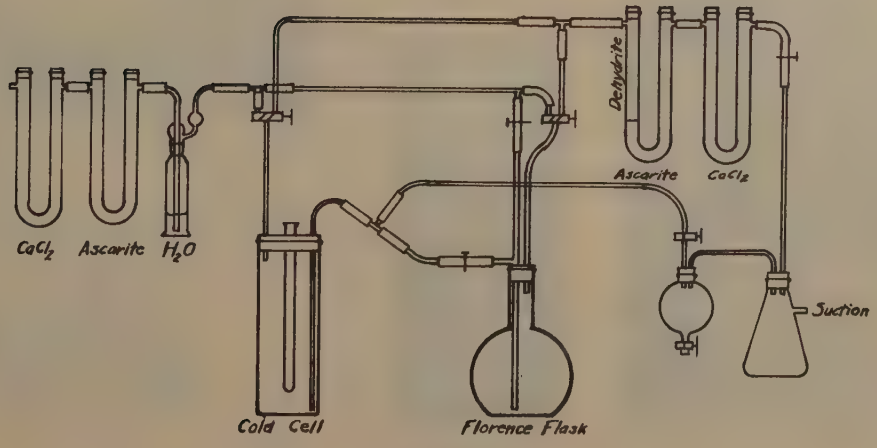


Fig. 22

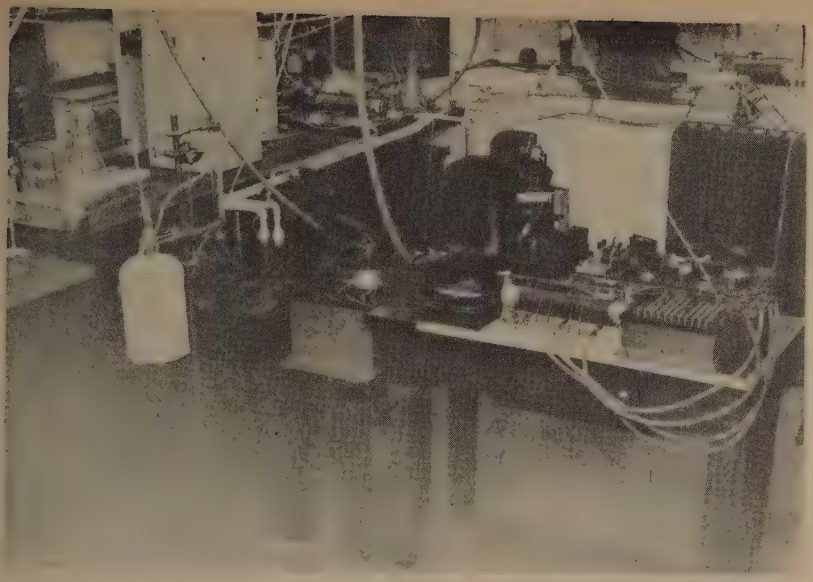


Fig. 17

Fig. 27

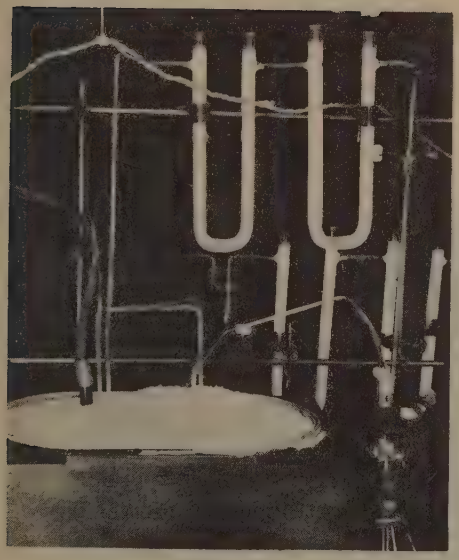


Fig. 23

Fig. 29

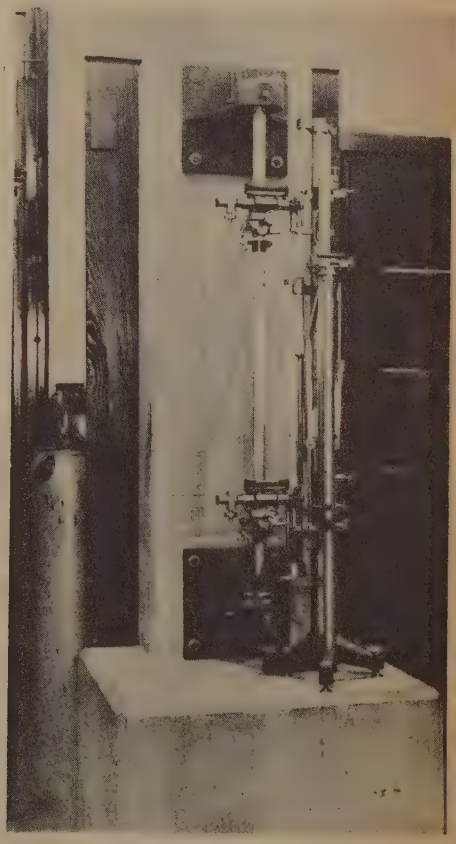


Fig. 28

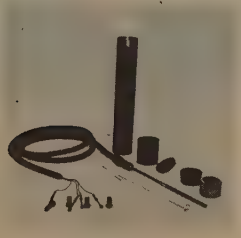


Fig. 25

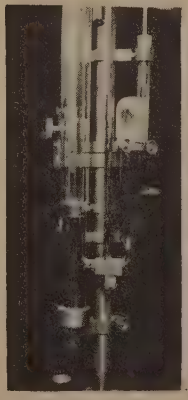
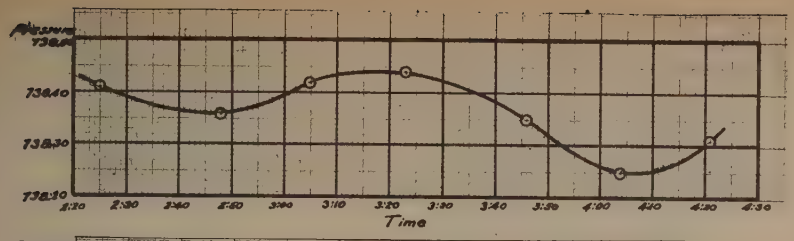
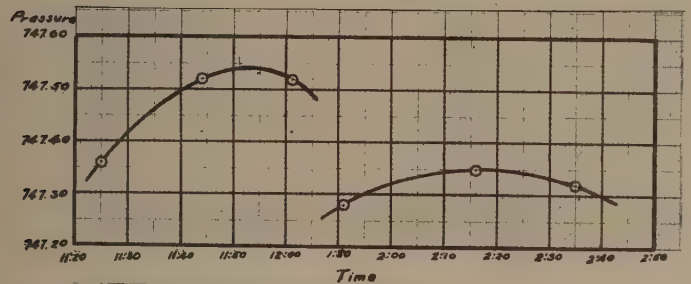


Fig. 30





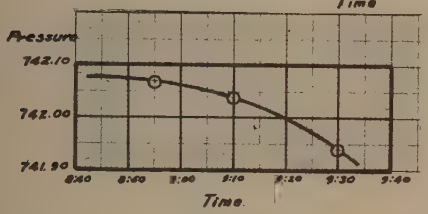


Fig. 35

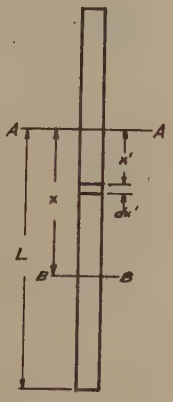


Fig. 34

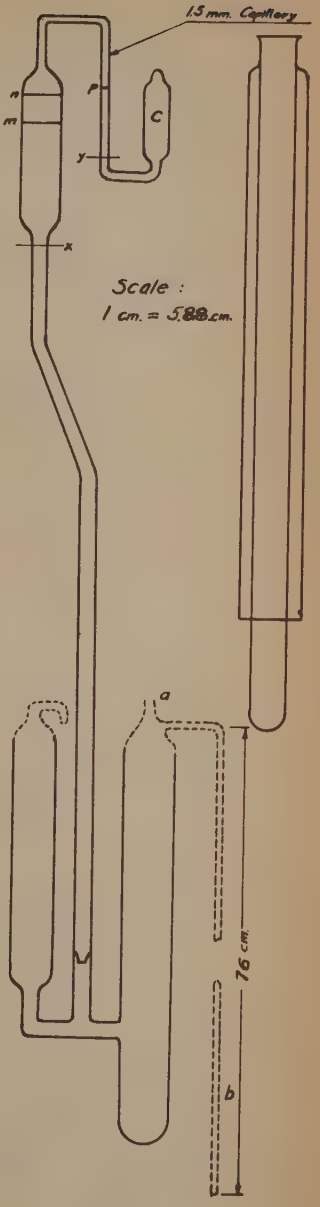


Fig. 31

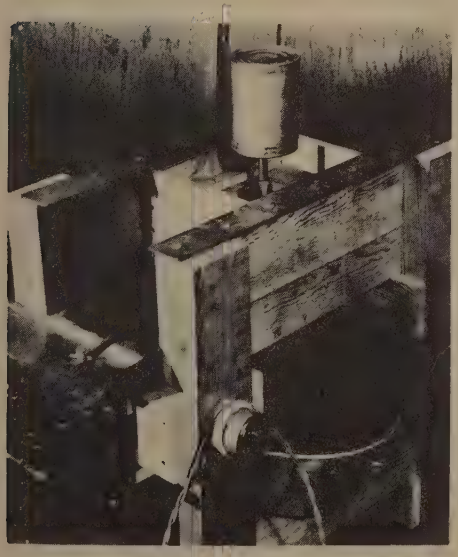


Fig. 24

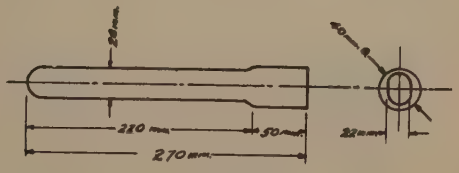


Fig. 26

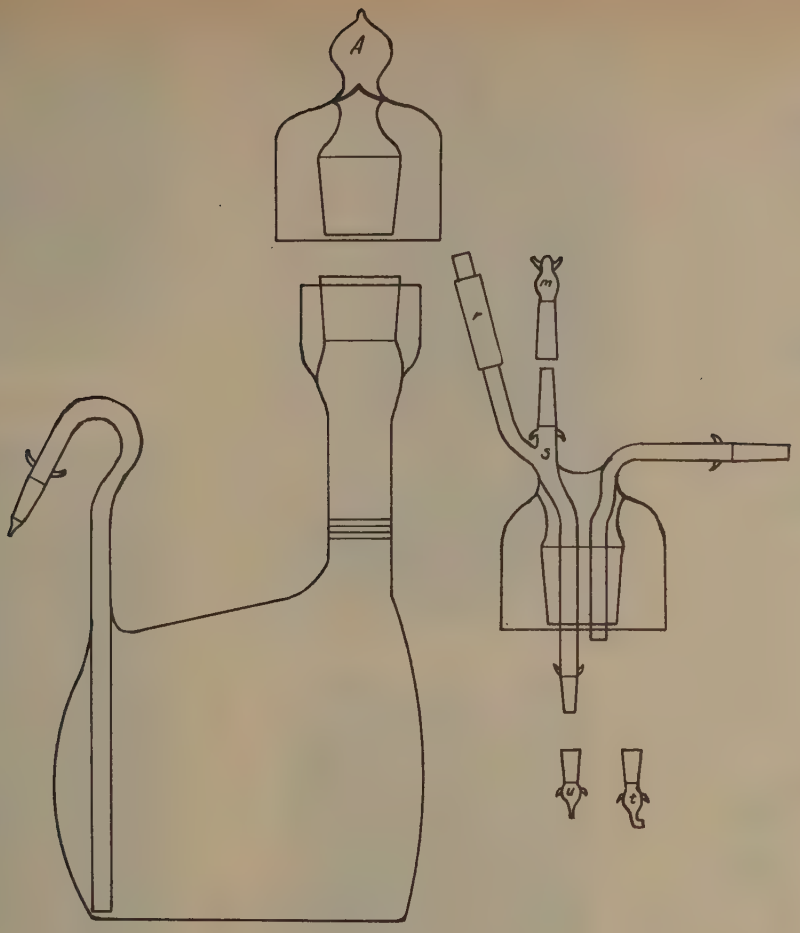

A
m
r
s
u
t

Fig. 36

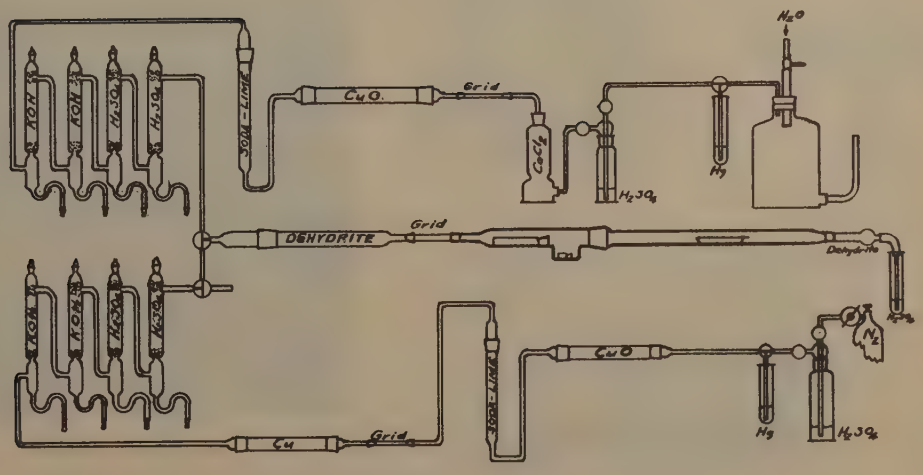

KOH
KOH
H_2SO_4
H_2SO_4
SODA-LIME
CuO
Grid
$CaCl_2$
H_2SO_4
Hg
H_2O
DEHYDRITE
Grid
Dehydrite
KOH
KOH
KOH
KOH
P_2O_5
N_2
CuO
SODA-LIME
Cu
Grid
Hg
H_2SO_4

Fig. 39

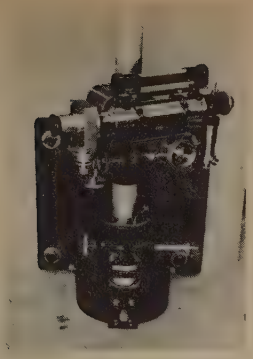


Fig. 32

Fig. 41

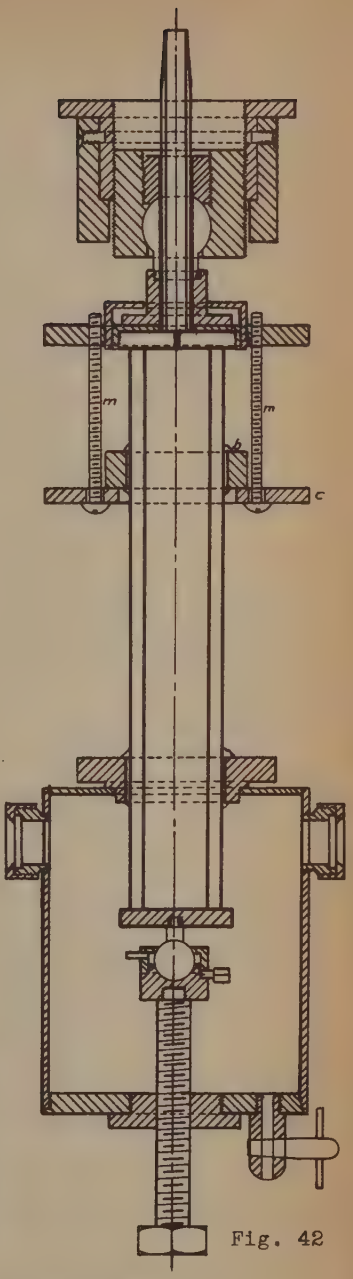


Fig. 42

Fig. 33

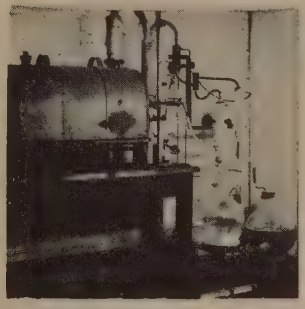


Fig. 37

Fig. 38

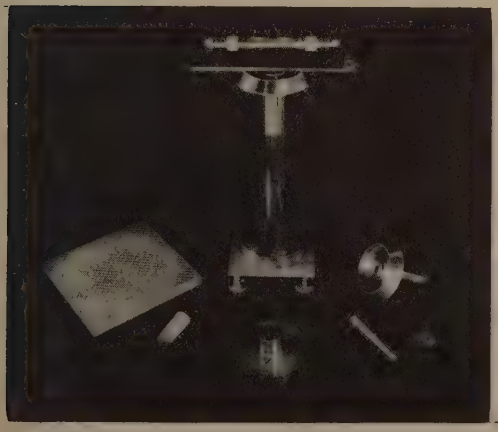


Fig. 40

Fig. 43

BIBLIOGRAPHY

1. Abbe, C., Annual Report of the Chief Signal Officer for 1887, part 2, U.S. Dept. of War.
1a. Archibald, E. H., "The Preparation of Pure Inorganic Substances", Wiley, (1932), 323.
2. Arrhenius, S., Bihang der Stockholmer Acad., 8, Nos. 13 and 14 (1883).
3. Buckingham, E., Bur. Standards Bull., 3, 237-293 (1907).
4. Burgess, G. K., B. S. J. Research, 1, 635-640 (1928).
5. Callendar, G. S., Phil. Mag., (7), 14, 729-742 (1932).
6. Callendar, H. L., Phil. Trans., A, 178, 161-230 (1887).
7. Callendar, H. L., Phil. Mag., (5), 32, 104-113 (1891).
8. Callendar, H. L. and Griffiths, E. H., Phil. Trans., A, 182, 119-157 (1891).
9. Curtis, H. L. and Grover, F. W., Bur. Standards Bull., 8, 495-517 (1912).
10. Dickinson, H. C. and Mueller, E. F., Bur. Standards Bull., 3, 641-661 (1907).
11. Dickinson, H. C. and Mueller, E. F., Bur. Standards Bull., 9, 483-492 (1913).
12. Eastman, E. D., J. Am. Chem. Soc., 42, 1648-1655 (1920).
13. Encyclopedia Brittanica, 11th ed., 38, 584.
14. Ferguson, A. L., Van Lente, K. and Hitchens, R., Ind. Eng. Chem., Anal. Ed., 4, 218-219 (1932).
15. Gray, A. W., Bur. Standards Bull., 10, 375-390 (1914).
16. Griffiths, E. H., Phil. Trans., A, 182, 43-72 (1891).
17. Griffiths, E. H., Phil. Trans., A, 184, 361-504 (1893).
18. Griffiths, E. H., Nature, 53, 39-46 (1895).
19. Grützmacher, F., Wiss. Abh. der Phys. Tech. Reichsanstalt, 3, 259-261 (1900).
20. Guillaume, C. E., Trav. et mem. du Bur. Int., 5, 37-40 (1886).
21. Gunn, R., J. Optical Soc. Am., 8, 545-547 (1924).
22. Hall, R. E. and Adams, L. H., J. Am. Chem. Soc., 41, 1515-1525 (1919).
23. Hildebrand, J. H., J. Am. Chem. Soc., 31, 933-935 (1909).
24. Hulett, G. A., Phys. Rev., (1), 33, 307-316 (1911).
25. I. C. T., 1, 393, 402 (1926).
26. I. C. T., 2, 458 (1927).
27. I. C. T., 3, 43 (1928).
28. I. C. T., 3, 87 (1928).
29. I. C. T., 6, 230-304 (1929).
30. Jessup, R. S. and Green, C. B., B. S. J. Research, 13, 469-495 (1934).
31. Johnson, C. R., J. Phys. Chem., 39, 791-795 (1935).
32. Jones, G. and Bollinger, D. M., J. Am. Chem. Soc., 57, 280-284 (1935).
33. Jones, G. and Bollinger, G. M., J. Am. Chem. Soc., 51, 2407-2416 (1929).
34. Jones, G. and Bollinger, G. M., J. Am. Chem. Soc., 53, 411-451 (1931).
35. Jones, G. and Bollinger, G. M., J. Am. Chem. Soc., 53, 1207-1212 (1931).
36. Jones, G. and Bradshaw, B. C., J. Am. Chem. Soc., 55, 1780-1800 (1933).
37. Jones, G. and Christian, S. M., J. Am. Chem. Soc., 57, 272-280 (1935).
38. Jones, G. and Josephs, R. C., J. Am. Chem. Soc., 50, 1049-1092 (1928).
39. Kohlrausch, F., Pogg. Ann. Jubelband, 290-303 (1874).
40. Kohlrausch, F., Wied. Ann., 11, 653-660 (1880).
41. Kohlrausch, F., Wied. Ann., 49, 225-256 (1893).
42. Kohlrausch, F., Wied. Ann., 56, 177-184 (1895).
43. Kohlrausch, F., Wied. Ann., 60, 315-332 (1897).
44. Kohlrausch, F. and Grotrian, O., Pogg. Ann., 154, 1-14, 215-239 (1875).
45. Kohlrausch, F. and Holborn, L., Das Leitvermögen der Elecktrolyte, B. G. Teubner, Leipzig, (1898).
46. Kohlrausch, F., Holborn, L. and Deisselhorst, H., Wied. Ann., 64, 417-455 (1898).

47. Kohlrausch, F., and Maltby, M. E., Wiss. Abh. der Phys. Tech. Reichsanstalt, 3, 156-227 (1900).
48. Kraus, C. A., Trans. Electrochem. Soc., 66, 178 (1934).
49. Kraus, C. A. and Dexter, W. B., J. Am. Chem. Soc., 44, 2468-2471 (1922).
50. Kraus, C. A. and Parker, H. C., J. Am. Chem. Soc., 44, 2422-2428 (1922).
51. Kueppers, K., U.S. Patent No. 1301714, April 22, 1919.
52. Marek, W. J., Trav. et mem. du Bur. Int., 1, D. 18 (1881).
53. Marek, W. J., Trav. et mem. du Bur. Int., 2, D. 11-12 (1883).
54. Marek, W. J., Trav. et mem. du Bur. Int., 2, D. 18-58 (1883).
55. Marek, W. J., Trav. et mem. du Bur. Int., 3, D. 22-51 (1884).
56. Marvin, C. F., Circular F, Instrument Division, U. S. Dept. of Agric., Weather Bureau.
57. Moon, C., B. S. J. Research, 14, 363-365 (1935).
58. Morgan, J. L. R. and Lammert, O. M., J. Am. Chem. Soc., 48, 1220-1233 (1926).
59. Mueller, E. F., Bur. Standards Bull., 13, 547-561 (1917).
60. Mueller, E. F. and Sligh, T. S., Jr., J. Optical Soc. Am., 6, 958-964 (1922).
61. Newberry, E., J. Chem. Soc., 113, 701-707 (1908).
62. Parker, H. C., J. Am. Chem. Soc., 45, 1366-1379 (1923).
63. Parker, H. C., J. Am. Chem. Soc., 45, 2017-2033 (1923).
64. Parker, H. C. and Parker, E. W., J. Am. Chem. Soc., 46, 312-335 (1924).
65. Pernet, J., Trav. et mem. du Bur. Int., 1, B. 1-52 (1881).
66. Pernet, J., with Jaeger, W. and Gumlich, E., Wiss. Abh. der Phys. Tech. Reichsanstalt, 1, 81-102 (1894).
67. Richards, T. W., Am. J. Sci., (4), 6, 201 (1898).
68. Richards, T. W., J. Am. Chem. Soc., 22, 144-149 (1900).
69. Richards, T. W. and Parker, H. G., Proc. Am. Acad. Arts Sci., 32, 59 (1896).
70. Richards, T. W. and Wells, R. C., Proc. Am. Acad. Arts Sci., 38, 431-440 (1903).
71. Rosa, E. B., Bur. Standards Bull., 5, 413-434 (1908).
72. Rosa, E. B. and Babcock, H. D., Bur. Standards Bull., 4, 121-140 (1907).
73. Shedlovsky, T., J. Am. Chem. Soc., 52, 1793-1805 (1930).
74. Shedlovsky, T., J. Am. Chem. Soc., 52, 1806-1811 (1930).
75. Shedlovsky, T., J. Am. Chem. Soc., 54, 1411-1428 (1932).
76. Siemens, C. W., Proc. Roy. Soc. (London), A, 19, 443-445 (1871).
77. Sligh, T. S., Jr., Bur. Standards Bull., 17, 49-63 (1922).
78. Smith, F. E., Phil. Mag. (6), 24, 541-569 (1912).
79. Taylor, W. A. and Acree, S. F., J. Am. Chem. Soc., 38, 2396-2403 (1916).
80. Taylor, W. A. and Acree, S. F., J. Am. Chem. Soc., 38, 2403-2415 (1916).
81. Taylor, W. A. and Acree, S. F., J. Am. Chem. Soc., 38, 2415-2430 (1916).
82. Thiesen, M., Scheel, K. and Sell, L., Wiss. Abh. der Phys. Tech. Reichsanstalt, 2, 138-142 (1895).
83. Vreeland, F. K., Phys. Rev., (1), 27, 286-293 (1908).
84. Wagner, K. W., Elektrotech. Z., 33, 635-637 (1912).
85. Waidner, C. W., Dickinson, H. C., Mueller, E. F. and Harper, D. R., 3rd, Bur. Standards Bull., 11, 571-590 (1915).
86. Washburn, E. W., J. Am. Chem. Soc., 38, 2431-2460 (1916).
87. Washburn, E. W. and Parker, K., J. Am. Chem. Soc., 39, 235-245 (1917).
88. Weatherill, P. F., J. Am. Chem. Soc., 52, 1938 (1930).
89. Wenner, F. and Weibel, E., Bur. Standards Bull., 11, 1-40 (1915).
90. White, W. P., J. Am. Chem. Soc., 36, 2011-2020 (1914).
91. White, W. P., J. Am. Chem. Soc., 56, 20-24 (1934).
92. Wien, M., Weid. Ann., 58, 37-72 (1896).
93. Wild, H., Repertorium für Meteorologie, St. Pétersburg, III, No. 1 (1874).
94. Wolff, F. A., Shoemaker, M. P. and Briggs, C. A., Bur. Standards Bull., 12, 375-464 (1916).